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PART III

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THERMOGRAVIMETRY OF PHENOL-FORMALDEHYDE POLYCONDENSATES

PART III. CARBON/GRAPHITE CLOTH REINFORCED COMPOSITES TO 1400°C

R. W. FARMER

TECHNICAL REPORT AFML-TR-65-246, PART III

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CLEARINGHOUSE
The Aerospace Corporation
P.O. Box 1217
Beverly Hills, California 90212

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by the Plastics and Composites Branch, and was initiated under Project No. 7340, "Nonmetallic Composites and Materials," Task No. 734001, "Thermally Protective Plastics and Composites." It was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, Mr. R. Farmer (MANC), Project Engineer.

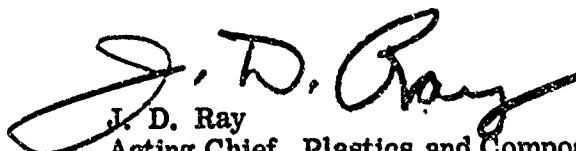
This report covers work conducted from March 1968 to September 1969. It was submitted by the author in September 1969.

Previous efforts related to this program may be found in AFML-TR-65-146, Parts I and II, and AFML-TR-68-184, Part I.

The author wishes to acknowledge with appreciation the valuable assistance and contributions of the following individuals: Dr. M. Manoff for computer code assistance; Mr. N. Olson for computer code design, sample preparation, and construction and operation of the recording thermo-balance; Mr. P. Pirrung for providing sample materials.

Many of the items compared in this report were commercial items that were not developed or manufactured to meet any Government specification, to withstand the tests to which they were subjected, or to operate as applied during this study. Any failure to meet the objectives of this study is no reflection upon any of the commercial items discussed herein or upon any manufacturer.

This technical report has been reviewed and is approved.


J. D. Ray
Acting Chief, Plastics and Composites
Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Carbon and graphite cloth reinforced phenolic composites find Air Force[®] ablative thermal protection uses as nose tips, heat shields, and rocket nozzle elements. Weight kinetics are used in predicting the performance of these and related materials. The most general source of the necessary kinetic parameters is thermogravimetry.

Kinetic parameters n , A , and E were empirically calculated for the pyrolysis of phenolic molding, phenolic/carbon cloth, and phenolic/graphite cloth materials. The simple model was

$$-(dw/dt) = w^n A \exp (-E/RT)$$

where w = normalized weight, t = time, R = gas constant, T = temperature.

The material was first pulverized by a lathe method. A -325 sieve, dried 40 or 80 mg powder was run at 8.5°C/min to 1400°C in a helium purge of 1 liter/min. An integral method computer code and a maximum rate of weight loss method computer code calculated n , A , and E . To define the gross sum of all errors, a third computer code was used to plot thermograms for comparison with the experimental.

The empirical kinetic parameters predicted thermograms within 2% residual weight of the parent one. Of three typical bands of disagreement, the largest usually occurred within the third band near 800°C. There was little weight loss beyond 1000°C for any material. The phenolic molding parameters were in good agreement with multiple heating rate and multiple materials results of previous work.

A two-step phenolic/carbon cloth thermogram was in part due to cloth pyrolysis with probable synergistic resin interaction. An averaged, one-step set of parameters gave better thermogram predictability. The graphite cloth was relatively inactive for the phenolic/graphite cloth composite.

The thermobalance was routinely operated to 1400°C using a furnace/controller/recorder system. A 2-pen $X-Y^1-Y^2$ recorder plotted the weight/temperature/time thermogram. The suspended spring balance, a thermocouple

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within the sample, a time base, and a vacuum/purge system provided good accuracy. A 2.4% by weight reproducibility was found for six runs of the phenolic molding.

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SYMBOLS

| SYMBOL | DEFINITION | SYMBOL UNITS |
|-----------------------|---|-----------------|
| A | empirical kinetic parameter | 1/min |
| E | empirical kinetic parameter | kcal/gm-mole |
| exp | exponential function to the base e | dimensionless |
| f | function | |
| k | empirical kinetic parameter | 1/min |
| K | integral parameter | dimensionless |
| ln () | logarithm to the base e | dimensionless |
| log ₁₀ () | logarithm to the base 10 | dimensionless |
| m | series term | dimensionless |
| n | empirical kinetic parameter | dimensionless |
| N | n | dimensionless |
| R | gas constant | kcal/gm-mole/°K |
| t | time | min |
| T | temperature, degrees absolute* | °K |
| TD | \dot{T}^* | °K/min |
| w | reactant (residue-free) weight fraction | dimensionless |
| w ₀ | aggregate sample weight fraction | dimensionless |
| WOI | w _{oi} | dimensionless |
| WR | w _r | dimensionless |

SUBSCRIPTS

| | | |
|---|--------------------------------|----|
| x | reactant (residue-free) weight | gm |
| c | calculated | |
| i | initial | |
| m | maximum rate of weight loss | |

*Different units for a symbol are noted with that symbol.

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SYMBOLS (CONTD)

| SYMBOL | DEFINITION | SYMBOL UNITS |
|--------|------------|--------------|
| r | residue | |
| 1, 2 | singular | |

SUPERSCRIPTS

| | |
|-----|-------------|
| ' | special |
| (') | $d()/dt^*$ |
| (') | $d()/dT^*$ |

FUNCTIONAL SYMBOLS

| SYMBOL | DEFINING EQUATION | SYMBOL UNITS |
|-----------------|--|---------------|
| A' | $-\dot{w}_{Tm} w^{-n} T \exp(X_m)$ | 1/min |
| a_o, b_o, c_o | $g = a_o n^2 + b_o n + c_o$ | dimensionless |
| g | $\sum (w_{oc} - w_o)^2$ | dimensionless |
| p(X) | $X^{-1} e^{-X} - \int_X^\infty X^{-1} e^{-X} dX$ | dimensionless |
| r | $X^2 e^X p(X)$ | dimensionless |
| w | $x/x_i = (w_o - w_r)/(w_{oi} - w_r)$ | dimensionless |
| X | E/RT | dimensionless |

*Different units for a symbol are noted with that symbol.

SECTION II

INTRODUCTION

Constant heating rate thermogravimetry is a useful laboratory tool for materials research and exploratory development. A recording thermobalance, programmed at a linear rate of heating, monitors sample weight during this dynamic experiment.

The successful aerospace use of thermosetting plastics and reinforced composites for adhesives, ablative thermal protection, radomes, or structural members has led to many thermogravimetric studies. Additive enhancement of a particular reaction, catalysis, kinetics and physicochemical mechanisms, purge gas type and pressure interactions, and thermal stability are frequent areas of study.

The thermogravimetry of plastics is unfortunately dependent upon procedural aspects in addition to the run variables of temperature, time, and weight. For example, a phenol formaldehyde powder, run in a near inert atmosphere, gives a thermogram like Figure 1. Sample weight and run time are shown here as a function of temperature over two sweeps of the thermogram. Part I of this report showed that a change in ambient pressure, initial sample weight, or particle size of the powder changed the shape of the thermogram. The effect was less pronounced when a percentage "ladder" was used; the "ladder rungs" of the initial weight-to-stable weight fraction was simply adjusted to "rungs" of 0-1. The normalized value was termed a residue-free weight fraction.

A proven ability of a residue-free basis to suppress procedural aspects has led to kinetic studies less biased by experimental technique. In Part II, the similarity of kinetic parameters for three phenol formaldehyde studies was encouraging evidence that a simple, residue-free kinetic model was probably empirically valid. As precise controlling physicochemical processes of pyrolysis were not known, the precise governing kinetic equations were not known either. Therefore, the efficient curve-fitting of the model was strictly empirical in nature.

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In this report, the thermogravimetry of pure and glass cloth-reinforced phenol formaldehyde resins has been extended to include carbon/graphite reinforced composites. A modified thermobalance provided good precision to 1400°C via a noble metal thermocouple residing within the sample, a furnace/controller/recorder system, a two-pen recorder, and other innovations (References 1 and 2). As an old phenol formaldehyde molding was also pulverized by a new lathe method and run by a new operator on this instrument, this gave a nearly independent evaluation of old data.

Empirical kinetic parameters were calculated using two computer codes from Part II of this report (MAXRAX and TRIM). A new and useful code, PAR 3, provided comparative thermograms from input empirical kinetic parameters.

Carbon and graphite cloth-reinforced composites find Air Force thermal protection applications as nose tips, heat shields, rocket nozzle elements, and related end-uses. Kinetic models have, with reservation, been used in predicting ablative performance. The extrapolation chasm from the simple thermogravimetry experiment to the complex internal pyrolysis zone of an ablating material amply justifies this reservation.

A current use of thermogravimetry empirical kinetic parameters to predict ablative performance is a result of a lack of better simulation methods. A base line of parameters is necessary, however, to meet this need, to aid in designing better methods, and to supplement these experiments when available. A first step in extending the existing base line is to obtain data for reinforced composites beyond the 1000°C limit of most previous work on pure resins.

Within the necessary but questionable practice of far ranging extrapolation, this report hopefully satisfies an immediate practical goal of high precision, base-line empirical kinetic parameters for carbon/graphite-reinforced composites to 1400°C. Advanced kinetics study could involve additive modification of main reactions, high heating rate, oxidation, pressure, reactive hot char, residence condition of the pyrolysis gas, and other more realistic simulation of the ablative environment.

SECTION II

EXPERIMENTAL MATERIALS

1. PHENOL FORMALDEHYDE MOLDING

The high density molding was prepared from RI4009 novolac resin made by the Monsanto Chemical Company (References 3 and 4). The commercial brown powder was about -400 sieve in particle size. About 9% by weight of hexamethylenetetramine reactant-catalyst was estimated to be present by elemental chemical analysis.

The molding was made in a small stainless steel jig (Table I). The loaded jig was processed at 320 psi for 30 minutes at 92°C with a gradual change over a 15-minute period to 160°C, which was held for 30 minutes. The post-cure temperatures of 150° and 178°C were for 24 hours each with the jig at a pressure of 320 psi.

2. CLOTH-REINFORCED MATERIALS

The carbon cloth- and graphite cloth-reinforced composites were made with CTL-91LD phenol formaldehyde resin, a product of CTL, Incorporated. The carbon cloth (CCA-1) and graphite cloth (G1550) were both products of H. I. Thompson Fiberglas Company.

The reinforced composites were prepared by the Hughes Aircraft Company using proven and standardized methods (References 5 and 6). A pre-preg was made by first drying the reinforcement, adjusting resin solids, coating the cloth, air drying, and then cyclic temperature staging of the resin (Table I). Shaped pre-preg was then loaded into a fixture for compression molding.

After molding and post curing, the composite laminate was machined into a specimen designed for hyperthermal ablative testing. Barcol hardness, density, and other properties were measured for the laminate or specimen.

Ablative materials codes were retained for this work. For example, for 9-35-C and 9-35-GU-1, the prefix 9 was indicative of the resin trade name; the hyphenated digits 35 gave the nominal percent-by-weight resin content; the letters C or GU designated carbon or graphite cloth, respectively; the numerical suffix was for a specific sample of a group.

SECTION III

EXPERIMENTAL PROCEDURES

1. RECORDING THERMOBALANCE

A modified Aminco Thermo-Grav recording thermobalance was used for routine constant heating rate thermogravimetry to 1400°C (Figures 2 and 3). This precision instrument and experimental procedures for its use have been previously described in detail (References 1 and 2). This section consists of a brief and convenient review of relevant functions and techniques.

The weight/temperature/time thermogram was automatically plotted by an X-Y¹-Y² recorder. During the run the stimulus of weight change moved two precision springs. A linear variable differential transformer (LVDT) response voltage drove one recorder pen. A novel platinum, platinum + 13% rhodium, platinum (ground) thermocouple gave the EMF to move the X-axis carriage. Run time was plotted by the Y² pen via a synchronous time base generator.

The balance suspension system included an adjustable top, two springs, a support rod with fixtures, and, at the far end, a thermocouple sheath with attached crucible. The system could be positioned by a micro adjuster at the top of the glassware. In a similar fashion, an LVDT micro device permitted critical adjustment of the coil. A Pyrex support rod, the central part of the system, was joined to the springs just below the spring chamber. The rod held an LVDT core, a weight pan, and an oil dashpot ring. The thermocouple sheath and crucible hung from the other end of the support rod. The crucible, furnace tube, and sheath were all made from recrystallized alumina.

The sample thermocouple feedthroughs — fine tungsten wire lead/mercury pool/tungsten electrode — had little mechanical effect upon suspension linearity. The thermocouple signal was further grounded and filtered to shield against noise pickup at high temperatures.

The spherical furnace was controlled by a time linear SCR power programmer. A strip chart recorder plotted a temperature/time history of the output of the Pt, Pt + 10% Rh furnace thermocouple.

The balance suspension system was enclosed within a Pyrex/metal/alumina envelope. All runs were made in helium flowing at slightly above atmospheric pressure. The envelope was initially purified by three consecutive evacuation and helium fill cycles at room temperature.

There were three water regulatory circuits. The temperature within the spring chamber was controlled by a water bath via circulation through a double-wall annulus. A chamber thermocouple and digital readout was used for temperature monitoring. The center periphery of the furnace was also water cooled to minimize cabinet heating. In addition, water cooling of two feed-through mercury pools reduced evaporation to a safe level.

2. THERMOGRAVIMETRY PROCEDURES

The standard run was for a -325 sieve, dried powder for the following nominal conditions: 8.5°C/min to 1400°C in a helium purge flowing at an inlet rate of 1 liter/min. The sample weights were 40 mg for the molding and 80 mg for the two cloth-reinforced composites. An analytical balance was used for weighing out the sample and weighing the run residue (± 1 mg).

The standard ranges for the X-Y¹-Y² recorder were 0 to 20 mg/5 in. , 0 to 1400°C/20 in. , and 0 to 200 min/5 in. (Figure 1). The weight abscissa of 4 mg/in. over 5 inches of chart, with a 40 or 80 mg sample respectively gave an easily read 50 to 100 or 75 to 100% of residual weight span. The thermogram ordinate of 0.8 mv/in. was convertible to a reference temperature (Table II). The reciprocal slope of the run time curve was the heating rate. As the two pens could not occupy the same spot, there was an X-axis time offset. This small correction was applied to run time readings.

Two full thermogram sweeps of weight, temperature, and time were made for high precision. To do this, the X-axis carriage was manually shifted back to zero after 10 inches of travel (to 806°C) for a total of 20 inches of chart (to 1402°C).

3. SAMPLE PREPARATION

A lathe was used for preparing sample powders. A -325 sieve yield of 75% plus was slowly machined from bulk stock by a tungsten dicarbide-tipped, "low bite" cutter.

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A surface layer was first removed from the material to avoid machining, postcure, or like defects (Reference 3). To deface, a vigorous initial sanding (240 or 400 grit silicon carbide paper) and towel wiping was followed by lathe surfacing. After up to four coarse passes, the piece was again cleaned thoroughly.

A chuck speed of 52 rpm was used with cut depths ranging from 0.001 - 0.003 inch to 0.0005-0.001 inch for surfacing and sampling, respectively. The cloth reinforced laminates were held with a three or four jaw chuck and machined parallel to the cloth plies. The RI4009 molding was bonded to an aluminum rod which in turn was mounted in a chuck.

The powder fraction was microscopically inspected for such quality indices as configuration, grain size, gross distribution, etc., before and after sieving. Fibrous material or a large +325 sieve fraction, considered indicative of possible resin content changes, was not apparent. The largely spherical particles visually appeared to be within a narrow size distribution.

All sieved sample powders were "dried" in a small vacuum oven for 50 minutes at 125°C and about 18 inches of Hg pressure. Without taking extreme precautions, every practical effort was made to minimize atmospheric exposure before or after a thermogravimetry run.

SECTION IV

COMPUTER CODES

1. EMPIRICAL KINETIC MODEL

The isothermal kinetic relations that were empirically forced to fit the thermogravimetry data were of the general form

$$-\dot{w} = kw^n \quad (1)$$

$$k = A \exp(-X) \quad (2)$$

The equivalent constant heating rate relation for Equations 1 and 2

$$-\dot{w}_T = (w^n A/\dot{T}) \exp(-X) \quad (3)$$

was rearranged as

$$K = -\int_1^w w^n dw \quad (4)$$

$$= (A/\dot{T}) \int_0^T e^{-X} dT \quad (5)$$

where K was a convenient functional symbol. Integration of Equation 5 by parts in two different ways gave

$$K = (AE/R\dot{T}) p(X) \quad (6)$$

$$p(X) = X^{-1} e^{-X} - \int_X^\infty X^{-1} e^{-X} dX \quad (7)$$

$$K = (AE/R\dot{T}) \left[1 - \sum_m (-1)^{m+1} X^{-m} (m+1)! \right] X^{-2} e^{-X} \quad (8)$$

For $m = 0$, a relative error was defined for the ratio of Equations 6 and 8

$$r = X^2 e^X p(X) \quad (9)$$

and gave an additional useful expression for K

$$K = r(AE/R\dot{T}) X^{-2} e^{-X} \quad (10)$$

(With the exception of PAR 3, the brief Section IV summary of the empirical model, general theory, and computer codes was extracted from the details of Parts I and II of this report.)

2. MAXRAX

The computer code MAXRAX calculated empirical kinetic parameters from maximum rate of weight loss experimental data. Essentially, the four equations

$$A = (w^{1-n} \dot{T} X / n T) e^X \quad (11)$$

$$E = -\dot{w}_T n R T^2 / w \quad (12)$$

$$n = \left[\ln [r(n^{-1} - 1) + 1] \right] / \ln w + 1 \quad (13)$$

$$r = X^2 e^X p(X) \quad (14)$$

were solved by an iterative procedure further using the tabulated tables

$$r = f_1(X) \quad (15)$$

$$w = f_2(n, r) \quad (16)$$

(where the subscript m was omitted for brevity). MAXRAX resulted from the maximum rate solution of Equations 1 and 2, namely, Equation 12. The other relations for A and n came from a comparison of Equation 12 with Equation 1, 2, and 10.

3. TRIM

TRIM calculated empirical kinetic parameters from integral weight fractions as a function of temperature. This integral method solved

$$\log_{10} (K/T^2) = (-E/R \ln 10)(1/T) + \log_{10} r(AR/E\dot{T}) \quad (17)$$

which was derived from Equation 10. The terms $(-E/R \ln 10)$ and $\log_{10} r(AR/E\dot{T})$ were made equal to a slope and intercept, respectively, for this nearly linear equation. A and E were estimated by the standard method of least squares. In operation, the observed weight fraction (w_0) was first converted to a residue-free weight fraction (w)

$$w = (w_0 - w_r) / (w_{0i} - w_r) \quad (18)$$

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and then a K value

$$K = -\frac{1}{n} w \quad \text{for } n = 1 \quad (19)$$

$$= (w^{1-n} - 1) / (n - 1) \quad n \neq 1 \quad (20)$$

for the MAXRAX n. Equations 19 and 20 were the solution of Equation 4.

TRIM incremental temperatures corresponded to 0.1 inch divisions of chart paper. As for conventional practice, small rate-of-weight loss points at the start and first sweep end of the thermogram were discarded. The useful "q temperature span" was estimated for each run (up to 99 points to 806°C).

The use of the standard method of least squares was an approximation for TRIM. All Equation 17 terms were interdependent, the experimental precision was variable, and the MAXRAX term r slowly decreased with increasing temperature (about $\pm 4\%$ maximum change within the q temperature span). Therefore, a second parameter A' was calculated from Equation 3 to compare with A

$$A' = -\dot{w}_T w^n \dot{T}_e X \quad (21)$$

for the maximum rate-of-weight loss point.

4. PAR 3

PAR 3 was a computer code for graphical construction of a thermogram from input empirical kinetic parameters. Equation 6 was solved via a p(X) table. A w value, from the converse of Equations 19 or 20, became a w_0 using the converse of Equation 18. Up to 199 weight fractions for 0.1 inch increments of chart from 14.4°C to 1396.4°C were graphed by an X-Y plotter. Derived in part from the construction subroutine of Part II of this report, PAR 3 proved uniquely helpful in kinetic studies; a future detailed report is planned for this code.

5. PRIM

PRIM, a revision of TAIL provided a "best" value of n with corresponding values of A and E. Briefly, six incremental values were chosen around the

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MAXRAX n result. TRIM was then repeated for these six values. An overall error term g

$$g = \sum (w_{oc} - w_o)^2 \quad (22)$$

was calculated for each case. A best value n' came from assumed g dependence upon n as

$$g = a_o n^2 + b_o n + c_o \quad (23)$$

using a parabolic method of least squares where n' was the ideal minimum of the curve. Two features of PRIM were two temperature spans and four indices of conformance between the calculated and experimental thermograms.

SECTION V

EXPERIMENTAL AND COMPUTER CODE RESULTS

1. PHENOL FORMALDEHYDE MOLDING

The greatest weight loss portion of the RI4009 thermogram closely resembled an arc tangent function. To evaluate reproducibility, six replicates were sketched together (Figure 4). The maximum weight spread of about 2.4% began near the end of the first carriage traverse and fluctuated slightly over the second sweep (800°-1400°C). There was a weight band of about 1.5% near the thermogram shoulder (300°C); run number 500 gave lower weights here. A similar fluctuating spread propagated down to 600°C. The constant weight temperature spread of about 100°C near 800°C rapidly increased for the nearly flat and parallel second sweep curves. Although the calculations were not made, the thermograms did appear more reproducible for a residue-free basis.

The relative position of six thermograms was not consistent from run to run below 800°C. Run number 539 gave the highest stability, or highest weight at constant temperature, to about 600°C. Run number 500, of lowest stability over the shoulder region, had by then crossed other runs for the highest weights to 1400°C. Run number 503 was least stable from about 530°C to 800°C; run numbers 503 and 520 merged just within the second sweep to be of lowest stability until the very end.

MAXRAX was used to calculate empirical kinetic parameters for the six replicate thermograms. The total spread in n , A , and E was relatively small (Table III). This increasing order of their uncertainty, as shown by the range of limiting values and the standard deviations, was consistent with general expectations.

There was a mutual compensation between n , A , and E . The tendency was for A and E to increase with an increase in n . This was consistent with Equations 12 and 13. The former showed E to be proportional to n . The latter indicated that although A was an inverse function of n , this was easily outweighed by an exponential dependence upon E . The other terms in the two equations were well reproduced upon the basis of inspection and standard

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deviations. Slight trends were, however, still apparent. For example w_m ideally varied with both n and r_m to nearly equal but opposite degrees. The results showed a small but still consistent increase in w_m and an increase in n with a decrease in r_m .

PAR 3 thermograms were plotted from the MAXRAX empirical kinetic parameters and compared with experimental ones for six replicate runs of RI4009. There were four bands of disagreement (Appendix I). Although the weight deviations of up to 2% were small compared to reproducibility and probable error, the repetitive nature of the bands suggested that they were real. First, the experimental thermogram was overpredicted by up to 1% to about 340°C. For run numbers 503, 506, and 529, the experimental result was briefly more stable by 0.6 to 1 percent. The experimental weights were less than calculated within the region of high weight loss of about 380° to 600°C. The fourth band began near 600°C with low calculated weights. This deviation steadily led up to 2% or so just before or after the pen shift.

The maximum deviation between calculated and experimental RI4009 thermograms ranged up to about 2% near the end of the first thermogram sweep. This was less than the maximum 2.4% reproducibility spread, which also occurred within the same region. Although a thermogram could be predicted with fair precision using its derived set of empirical kinetic parameters, it was clear that much larger deviations would occur if another set or, say, the mean values for the six runs were used for this purpose.

TRIM calculations were made for a representative RI4009 case, run number 520 (Figure 5). MAXRAX, which used four indices at the maximum rate point plus the residual weight, showed better overall agreement than TRIM, which involved 67 data points from 325° to 800°C. TRIM generally predicted high weights. The maximum calculated-experimental weight differences were about 2 and 2.5% for MAXRAX and TRIM, respectively. Interestingly, the deviation for TRIM was small within the shift region.

TRIM calculations were also made for n values of unity and two in addition to the MAXRAX result of 1.36786. As for MAXRAX, the TRIM parameters A and E likewise increased with any increase in n (Table IV). The n values of

unity and two for TRIM predicted more and less stable thermograms, respectively, than found either experimentally or for MAXRAX. Although the calculations were not made, the best overall curve fitting was expected for MAXRAX, rather than TRIM, for the other five RI4009 runs.

A phenol formaldehyde molding was run at three heating rates and analyzed by means of MAXRAX, TRIM, and PRIM under Part II of this report. The three runs were averaged with other PRIM results to give a survey of six runs by three workers using four materials (Table V). Mean values of the empirical kinetic parameters for the three heating rates, survey, and current six replicate run cases were plotted via PAR 3 and intercompared with RI4009 run number 520 (Figure 6). The large spread between the thermograms was discouraging. Noting, however, the deviations in mean values of heating rate and residual weight, a reasonable adjustment was made to the rate and weight values for run number 520. All thermograms then agreed well, nearly approaching RI4009 reproducibility (Figure 7).

Three sets of empirical kinetic parameters gave thermograms within 4% residual weight of an RI4009 run. This degree of agreement strongly implied that the empirical kinetic model was probably valid. As the parameters were also previously representative for 6 other materials, either by calculation or residue-free analogy, 13 experiments by 4 investigators using 11 cured polycondensate powders have been shown to be consistent within a few percent of residual weight. (A detailed review of pure and reinforced phenolic materials thermogravimetry will be the object of a forthcoming part of this report.)

2. CLOTH-REINFORCED MATERIALS

The thermograms for the phenolic/carbon cloth (9-35-C) and phenolic/graphite cloth (9-35-GU-1) samples strongly resembled each other as well as those of RI4009 (Figure 8). About 65% by weight of relatively stable cloth within the composites resulted in lower total weight loss than for RI4009. The 9-35-C material underwent uniquely high weight losses at low temperatures in addition to a discontinuous, two-step pyrolysis mechanism.

A MAXRAX/PAR 3 thermogram, adjusted to average out the two-step irregularity for 9-35-C, agreed within 1.2% of the experimental run. This

approach gave better agreement than the attempt to separately describe the two steps. For the average approach, there were three bands of disagreement located just before the shoulder, just after the shoulder, and within the pen shift region.

Three predominate regions of MAXRAX/PAR 3 calculated-experimental thermogram differences were also found for 9-35-GU-1. A weight difference of about 0.3% was typical except at the lowest temperatures; a maximum deviation of 0.8% was evident here. The overall fit was considerably better than for 9-35-C.

TRIM/PAR 3 calculations were made for both 9-35-C and 9-35-GU-1. Values of n of unity and two were run together with the MAXRAX n result to study this variable (Figures 9, 10 and 11). All the TRIM fits to the 9-35-C thermogram were poor. The 9-35-GU-1 TRIM comparison for the MAXRAX n was more reasonable. For the three characteristic weight difference regions, the maximum deviation was about 1% near the maximum rate-of-weight loss point. TRIM n values of unity and two gave much higher deviations.

Residue-free thermograms were prepared from MAXRAX empirical kinetic parameters to help assess the role of the phenol formaldehyde resin within 9-35-C and 9-35-GU-1 (Figure 12). A residue-free basis effectively subtracted the highly stable graphite cloth weight for 9-35-GU-1 and the carbon cloth weight for 9-35-C once cloth pyrolysis had decayed near 500°C. An agreement of the RI 4009, 9-35-C, and 9-35-GU-1 thermograms within about 9% by weight was truly remarkable. The results suggested no important physicochemical effect for the graphite cloth within 9-35-GU-1. This comparison alone did not reveal any carbon cloth effect for 9-35-C as the MAXRAX parameters averaged out the two-step mechanism for this material.

Even though the molding, phenolic/carbon cloth, and phenolic/graphite cloth thermograms nearly collapsed into each other for a residue-free basis, there was still a wide spread for their empirical kinetic parameters (Table IV). As for RI4009, there was a clear mutual compensation tendency between n , A , and E for the MAXRAX results. The TRIM parameters covered three values of n from unity to two with corresponding changes between A and E .

The parameter A' was a check on the use of the method of least squares for TRIM. This hybrid parameter used both maximum rate-of-weight loss data and the TRIM value of E . In addition to being intermediate between A for MAXRAX and A for TRIM, the TRIM A' and E values were closest to the MAXRAX A and E than for any other TRIM case. Therefore, even though A' occasionally ranged up to nearly twice the TRIM A , this was easily due to a high sensitivity to E and the TRIM calculation was still considered confirmed in relative terms. A' was probably more precise than the TRIM A and thermogram fits using A' may have been better. In any event, TRIM tended to be weighted near the end of the first sweep of the thermogram by the choice of the q temperature span. By inspection, this also implied lower TRIM values of A as compared to A' , which was the case.

MAXRAX empirical kinetic parameters were calculated for three 9-35-C cases: step 1 ending at 480°C, step 2 from 480°-1400°C, and an average using step 2 data (Table VI). The latter set gave the best fit to the experimental thermogram. The two-step discontinuity of only about 0.8% maximum weight displacement was small compared to curve-fitting precision, readability of the thermogram, and reproducibility. Irrespective of these difficulties, an approximate attempt was made to calculate the thermograms for the two steps and fit them together as consecutive, independent reactions. The curves did not fit smoothly because the kinetic contact and reaction end points were not the same as the optimum curve-fitting contact and end points. The step 2 thermogram was then displaced along the weight axis until contact was made. The corresponding value of w_{oi} was then used to plot the curve again. The second fitting gave only a small error for the final residual weight w_r (Figures 13 and 14). Of several approximation methods tried, this juxtaposition was the most successful for smoothly combining the independent curves. The calculations for this purpose further revealed an anomaly in theory. An early portion of the step 2 thermogram gave weights increasing with temperature (Figure 14). This resulted from the fact that reactions were permitted at all temperatures other than absolute zero rather than starting at an assigned temperature. The artifact was rarely found and did not affect the calculated curve after w_{oi} was reached.

Although both carbon cloth and graphite cloth thermograms proved difficult to reproduce, two were chosen as being preliminary and tentative (Figure 15). Using the original resin content of the composite, ideal 9-35-C and 9-35-GU-1 thermograms were calculated as the corresponding adjusted sums of the R14009/CCA-1 and R14009/G1550 thermograms (Figures 16 and 17). The calculated R14009/CCA-1 thermograms was considerably less stable than the experimental result. The reason was not known. Speculatively speaking, there was a possibility of a synergistic effect of the cloth on resin pyrolysis. The effect could have either suppressed resin pyrolysis and/or oriented pyrolysis to leave a higher percentage of stable product. A similar tendency was found for the calculated R14009/G1550 thermogram. Within the precision of the necessary measurements, it was difficult to say if the apparent effect was real. In further analysis, the calculated 9-35-C final resin weight (or char yield) was considerably above that estimated for 9-35-GU-1 (Table VII).

In order to better understand the mutual compensation tendency between n , A , and E , a brief empirical kinetics parametric study was made, a portion of which was summarized as Figure 18. The study revealed that compensating sets of n , A , and E could easily approximate the same thermogram, particularly over narrow ranges of temperature at the higher temperatures.

SECTION VI

ACCURACY, PRECISION, AND SENSITIVITY

1. HEATING RATE

The heating rate was simply calculated as the ratio of temperature to corrected run time. This was the most reliable method of several tried (References 1 and 2). A deviation of less than $\pm 1^\circ\text{C}/\text{min}$ was found for averaging line tangents drawn along the minimum and maximum points of the temperature-time limits of two runs (Figure 19). The two runs bracketed a total of nine runs. This fluctuation between two linear heating rates was not the maximum nonlinearity error at any temperature.

Heating rate errors were further assessed using the average heating rate \dot{T} to 1400°C and the heating rate \dot{T}_m at the maximum rate-of-weight loss point. \dot{T} was used for TRIM and PAR 3; \dot{T}_m served as a MAXRAX input. The difference between the two approached the maximum nonlinear error (Figure 19). This difference ranged from 1.7° to $2.0^\circ\text{C}/\text{min}$ for the six RI4009 runs (Table III). The maximum weight difference of 0.75% between calculated-experimental thermograms was indicative of the maximum possible nonlinearity error near the maximum rate-of-weight loss point.

The relative fluctuations in heating rate were found to be consistent with deviation bands between calculated and experimental thermograms. For example, the true heating rate was below the mean up to about 340°C , or the shoulder for an RI4009 run. There was an increase in rate around 600°C , the beginning of the second area band. Finally, there was a rapid rate increase near 800°C , where large deviations occurred. These three error bands were consistent with the over-, under-, and under-prediction of the experimental RI4009 thermogram. To bracket errors due to heating rate fluctuation, thermograms were plotted for RI4009 run number 520 for $\dot{T} = 8.55^\circ\text{C}/\text{min}$ and $\dot{T}_m = 10.34^\circ\text{C}/\text{min}$ (Figure 20). The maximum weight difference of about 2.5% was near the maximum rate-of-weight loss region. The maximum reproducibility spread for six runs was 2.4% near the shift point. Further, the maximum calculated-experimental difference for the six runs was 1.5%. These comparisons suggested that heating rate fluctuations were a real if small contribution to all deviations.

In addition to the expected requirement for good residual weight and temperature accuracy, the importance of a linear heating rate was shown by a simple rearrangement of Equation 12

$$E = -\dot{w}nRT^2/\dot{w}\dot{T} \quad (24)$$

(where the subscript m was omitted for brevity). The parameter A was an exponential function of E and its error; n was less sensitive to errors. Although only applying at the maximum rate-of-weight loss point, Equation 24 was an approximation for this general region of the thermogram.

2. END OF RUN

The furnace controller was preset to shut off near 1400°C to end the run. For cases where shutoff occurred slightly early or late, an extrapolation was made to 1400°C for consistency.

The residual sample weight was estimated after a run by weighing. Table VII revealed that the weights usually agreed within 2.2% with the analytical balance result usually being low. Moisture content change or handling loss were possible error sources. Room humidity or sample absorption changes could have affected weighing either way with the latter error being more likely than the former. Sample loss during removal of the thermocouple gave a low final weight.

Little sample pyrolysis occurred after furnace shutoff. The sample cooled very rapidly. Occasional following of the weight cooling curve gave a slight weight increase drift, presumably a reverse of a heating weight error. For example, the weight loss was zero for the first pen sweep for a standard run on graphite powder. A weight loss of 0.25% for the second sweep, tentatively attributed to second order effects as local temperature variation around critical components, was essentially regained during cooling. The final analytical balance weight loss was 0.25%, an unexplicable value unless due to handling or humidity error.

The elapsed time at the thermogram shift point and the end of the run — from the chart, a digital readout, the furnace programmer, and a wall clock — helped confirm proper thermobalance operation. The corresponding sample and furnace temperatures were further spot checks. The temperature drift of the

spring chamber readout and a thermometer positioned with the stem near the center of the system envelope were further indicative of possible error due to system overheating. Other reliability indicators were also recorded at the beginning of the run, end of the run, and at the shift point. These have been reviewed along with other error sources within the thermobalance report (Reference 1).

Although the thermobalance was of high precision, it was not completely reliable. Of a total of fifty runs for the materials of this report and other samples, 35 were acceptable with a total of 5 additional runs being for calibration purposes only. Thermocouple failure was the most common cause of run rejection. Thermocouple anomalies and improvement suggestions have been previously reviewed (Reference 1).

3. PURGE GAS SYSTEM

The inlet helium purging flow was about 1 liter/min (1 atm, 25°C). This was not the effective flow rate pass the sample. It was necessary to position the furnace tube exhaust nipple just above the furnace. There were probably erratic flow patterns between the cold, inlet helium and the hot pyrolysis gases. The crucible, well down within the furnace hot zone, was within a regime of relatively uniform gas temperature if not composition. Although the effect of mass transfer rates on pyrolysis physicochemistry was unclear, little effect of flow rate from 0.2 to 4 liter/min was reported for the constant heating rate thermogravimetry of a phenolic/cork composition (Reference 7). This was suspected to be the case for phenol formaldehyde and other reinforced composite materials.

Three evacuation/refill cycles were made at room temperature to reduce oxygen contamination during helium thermogravimetry. Thermograms for graphite powder suggested only minute if any weight loss within their readability. The pressure at room temperature cleanup was read by an air thermocouple gauge. While correct in relative units, the values were not adjusted for the near helium atmosphere after the first cycle.

4. CALCULATED AND EXPERIMENTAL THERMOGRAMS

It was apparent that the analyses and presentation of thermograms on a total weight rather than residue-free basis could be misleading. The differences

between calculated and experimental thermograms were thus suppressed by a factor of about two for RI4009 and about three for the other materials. On the other hand, any application of the empirical kinetic parameters appeared likely to be for a total weight basis. Further, total weights were for the real life experiment and reproduction of the experimental landscape was a goal of this report. A partial compromise was made, in a sense, by summarizing the more valid empirical kinetic results on a residue-free basis for one case (Figure 12).

Copies of representative thermograms were included herein for possible close inspection by interested readers (Appendix II). It unfortunately proved necessary to retouch them, for reproduction and printing, of course, further reduced authenticity. The technique used to copy other curves was to first make a light pencil tracing on the PAR 3 graph paper. The tracing was later inked in by the artist for reproduction.

The thermobalance was operated at an upper limit in terms of inches of thermogram. The weight scale of 4 mg/in. and equivalent temperature scale of 0.8 mv/in. were almost the maximum available without using accessory amplifiers or other means. A practical crucible size and configuration dictated the sample weight. Although more sensitive time spans were available, 40 min/inch was a good compromise.

The readability of the plotted and recorded thermograms was about ± 0.15 weight percent, depending upon how the ink flowed that day. In practice, readings were taken at either the top or bottom of the curve. For the particularly difficult readings of temperature and corrected time for heating rate, the worse case of a high value was used if readability was low. The maximum error was in the order of $0.2^{\circ}\text{C}/\text{min}$.

The calculation of significant digits for the empirical kinetic parameters proved a difficult task. Therefore, all read and computer calculated digits were reported and used for further calculations. The only exception for this general rule was a limitation on PAR 3 of four digits for n with A being limited to five digits when expressed as a power of 10.

5. RECORDER CALIBRATION

The three axes of the recorder were periodically calibrated to be accurate within the manufacturer's absolute specifications. Although accessory calibrations have been reviewed in detail, the more important warrant a brief description (References 1 and 2). The sample temperature at the start of the run was registered by shorting out the thermocouple (at the ice bath) with the pen at zero. A three- or five-point calibration was made of the weight axis with the sample within the crucible. This was done by dropping weights upon the calibration pan and adjusting the span as necessary. The time base was calibrated by direct check with a stopwatch.

SECTION VII

SUMMARY AND CONCLUSIONS

Constant heating rate thermogravimetry was conducted to 1400°C for phenolic molding, phenolic/carbon cloth, and phenolic/graphite cloth materials.

A maximum rate-of-weight loss computer code (MAXRAX) and an integral method computer code (TRIM) were used to calculate empirical kinetic parameters. The four MAXRAX inputs were for the maximum rate point; TRIM used 67 weight-temperature data points. MAXRAX predicted more reproducible thermograms than TRIM. The thermograms were calculated and ultimately plotted by a third code (PAR 3).

The MAXRAX empirical kinetic parameters gave calculated-experimental weight differences of 2% or less for six molding runs. The maximum deviation occurred around 800°C. The six runs were experimentally reproduced within 2.4% of residual weight.

Molding thermograms based upon empirical kinetic parameters for the six runs, three heating rates, and a six-run materials survey did not exceed 4% spread in weight. The latter two sets of parameters were from previous work.

The phenolic/carbon cloth composite underwent a discontinuous, two-step pyrolysis. An average set of empirical kinetic parameters, which neglected the first step, gave a calculated thermogram within 1.2% by weight of the experimental. The phenolic/graphite cloth composite thermogram was fitted within 0.8 weight %.

Residue-free basis thermograms for the molding and phenolic/graphite cloth materials implied no graphite cloth effect during thermogravimetry. The carbon cloth role within the phenolic/carbon cloth composite was not clear.

The disagreement between the calculated and experimental thermograms usually occurred over three major regions: before and just after the shoulder of the thermogram and near the shift point of 800°C. There was a consistent mutual compensation tendency between the empirical kinetic parameters n , A , and E ; an increase in n gave a corresponding increase in A and E .

SECTION VIII

SUGGESTIONS FOR FURTHER WORK

Parts I and II of this report outlined a plan for possible further work in the thermal analysis of reinforced plastic composites. Some critical areas of potential work were again reviewed for this report with emphasis upon a need for (a) data for new materials, and (b) better simulation of aerospace environments.

There are a variety of promising polyaromatic and polyheterocyclic resins for which definitive kinetic information appeared desirable to aid ablative, coating, structural, and other aerospace uses. Classes of interest included modified phenol formaldehydes, polybenzimidazole, polyphenylene, polyquinoxaline, and polyimide.

Additional thermal analysis methods promised to help interpret kinetics and gross physicochemical mechanisms for resins and composites. Differential thermal analysis was of interest for both this purpose and to provide relative heats of pyrolysis. Heats of pyrolysis were applied in predicting ablative performance.

Thermogravimetry at high heating rates promised to be a better approximation to ablative and other aerospace environments. A systematic study of heating rate was desirable to determine the range of validity of the kinetic model and provide, if necessary, substitutes beyond its limits. Isothermal thermogravimetry was a further logical choice of an auxiliary experiment for model work. It was also clear that small, solid composite samples should be investigated in addition to powders.

An improved computer program was obviously a desirable aid for the calculation of empirical kinetic parameters. It was further obvious that the program should evaluate absolute, uncompensated values of n , A , and E in a least mean squares sense as well as provide temperature variance options for these three parameters. Temperature-dependent parameters appeared necessary to represent kinetics at high heating rates or under other severe conditions.

With either an advanced computer program or continuing use of the current codes, weight loss-rate data was a reasonable goal. An electronic differentiation apparatus was a desirable accessory for the recording thermobalance.

The influence of the purging gas over a wide range of flow rates and pressures was a further interesting investigative area. In particular, the effect of oxygen on heat transfer and kinetics at surfaces under low pressure was an apparent requirement for the prediction of ablative performance and optical/radar observables at high altitudes.

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TABLE I
EXPERIMENTAL MATERIALS

A. Sample Description

| | | | |
|--------------------|---------|--------------|----------------|
| Code | Molding | 9-35-C | 9-35-GU-1 |
| Reinforcement | none | carbon cloth | graphite cloth |
| HAC Data Sheet No. | none | 500 | 418 |

B. Pre-Preg Processing

Reinforcement Drying

Time, hr @ Each
Temperature, °C

2-116

2-116

Resin Dilution

Agent
Resin/Agent Ratio

acetone
1/0.5

acetone
1/0.7

Pre-Preg

Coating Method
Staging Time, hr @
Each Temperature, °C

brush

lab coater^f

Cycle 1^a

1-RT

?-116

2

1-71

3

0.3-107

C. Processing

Cure

Contact Time, min
Pressure, psi
Time, hr @ Each
Temperature, °C

320
0.5-92;
0.5-160

5
300
3-149

5
10000
2-149

Post-Cure

Cycle Code^b
Machined?^c
Number of Parts^c

none^g
no

B
yes
30

B
no

D. Post-Cured Laminate

Barcol Hardness
Density, gm/cc^d
Number of Plies^d
Overall Dimensions, inch^d
Resin Content, %^e
Specimen Type
Void Content, %^e

0
1.18
1x4x0.125
100
flexural
nil

70
1.38
52
16.75x18x0.5
37.9
hot gas flow
22.3

38
1.31
207
1.68x2.33
36.3
pipe

TABLE I (CONTD)

E. Resin Content and Weight History

| Code Item | Molding | 9-35-C Grams | % RC | 9-35-GU-1 Grams | % RC |
|-----------------|---------|-----------------|------|--------------------|------|
| Reinforcement | | 2769.9 | 0 | 1348.2 | 0 |
| Staging Cycle 1 | | 5211.3 | 45.8 | 2185.2 | 38.3 |
| 2 | | 4834.5 | 42.7 | | |
| 3 | | 4669.1 | 40.7 | | |

Molded Laminate

| | | | | | |
|-----------------------------------|--|--------|------|-------|------|
| Pre-Preg | | 4642.0 | 40.7 | 116.6 | 38.3 |
| Laminate | | 4590.0 | 40.0 | 116.1 | 39.2 |
| Machined Parts | | 4148.5 | 40.0 | | |
| Post-Cured Laminate (Or Parts) | | 4008.0 | 37.9 | 110.9 | 36.3 |

F. Trade Names^h

| | | | |
|---------------|--------|----------|----------|
| Reinforcement | | CCA-1 | G1550 |
| Resin | RI4009 | CTL-91LD | CTL-91LD |

| | | | |
|---------------|---------------|------------|------------|
| G. References | Farmer (3, 4) | Kimmel (6) | Kimmel (5) |
|---------------|---------------|------------|------------|

^aRT - air dried at room temperature.

^bPost-cure cycle B: 18 hr @ 135°, 72 hr from 135° to 204°, 4 hr @ 204°, 7 hr cooling to below 93°C.

^cThe large laminate was cut into parts to reduce the possibility of blowup during post cure.

^dNumber of plies in the thickness direction prior to machining laminate into parts or a specimen. The final dimension refers to thickness.

^eResin content (RC) by weight percent of resin. Void content by volume percent of voids in the resin. Resin content of post-cured laminate assumed unchanged during machining; resin content of the final pre-preg assumed unchanged until molding.

^fThe cloth was coated and staged in a laboratory coater. The tower temperature was 116° and the cloth speeds were 12 in./min and 16 in./min for runs 1 and 2, respectively; 207 each plies of runs 1 and 2 were randomized; the mixture was divided into two equal parts for molding two laminates.

^g24 hr @ 149°, 24 hr @ 177°C.

^hCCA-1, G1550 - H.I. Thompson Fiberglas Company. CTL-91LD - CTL, Incorporated. RI4009 - Monsanto Chemical Company.

TABLE II

THERMOGRAM X-AXIS DEFLECTION/TEMPERATURE CONVERSION

| DEFLECT (in.) | TEMP (°C) | TEMP (°K) | DEFLECT (in.) | TEMP (°C) | TEMP (°K) |
|------------------|--------------|--------------|------------------|--------------|--------------|
| 0.0 | 0.0 | 273.16 | 4.0 | 380.6 | 653.76 |
| 0.1 | 14.4 | 287.56 | 4.1 | 388.4 | 661.56 |
| 0.2 | 28.0 | 301.16 | 4.2 | 396.2 | 669.36 |
| 0.3 | 41.0 | 314.16 | 4.3 | 404.0 | 677.16 |
| 0.4 | 53.5 | 326.66 | 4.4 | 411.7 | 684.86 |
| 0.5 | 65.5 | 338.66 | 4.5 | 419.4 | 692.56 |
| 0.6 | 77.1 | 350.26 | 4.6 | 427.0 | 700.16 |
| 0.7 | 88.4 | 361.56 | 4.7 | 434.6 | 707.76 |
| 0.8 | 99.3 | 372.46 | 4.8 | 442.2 | 715.36 |
| 0.9 | 109.9 | 383.06 | 4.9 | 449.8 | 722.96 |
| 1.0 | 120.3 | 393.46 | 5.0 | 457.3 | 730.46 |
| 1.1 | 130.4 | 403.56 | 5.1 | 464.9 | 738.06 |
| 1.2 | 140.3 | 413.46 | 5.2 | 472.4 | 745.56 |
| 1.3 | 150.1 | 423.26 | 5.3 | 479.9 | 753.06 |
| 1.4 | 159.9 | 433.06 | 5.4 | 487.4 | 760.56 |
| 1.5 | 169.5 | 442.66 | 5.5 | 494.9 | 768.06 |
| 1.6 | 178.8 | 451.96 | 5.6 | 502.3 | 775.46 |
| 1.7 | 188.1 | 461.26 | 5.7 | 509.7 | 782.86 |
| 1.8 | 197.2 | 470.36 | 5.8 | 517.0 | 790.16 |
| 1.9 | 206.3 | 479.46 | 5.9 | 524.3 | 797.46 |
| 2.0 | 215.2 | 488.36 | 6.0 | 531.6 | 804.76 |
| 2.1 | 224.1 | 497.26 | 6.1 | 538.9 | 812.06 |
| 2.2 | 232.9 | 506.06 | 6.2 | 546.1 | 819.26 |
| 2.3 | 241.6 | 514.76 | 6.3 | 553.3 | 826.46 |
| 2.4 | 250.2 | 523.36 | 6.4 | 560.5 | 833.66 |
| 2.5 | 258.7 | 531.86 | 6.5 | 567.6 | 840.76 |
| 2.6 | 267.2 | 540.36 | 6.6 | 574.8 | 847.96 |
| 2.7 | 275.6 | 548.76 | 6.7 | 582.0 | 855.16 |
| 2.8 | 284.0 | 557.16 | 6.8 | 589.1 | 862.26 |
| 2.9 | 292.3 | 565.46 | 6.9 | 596.2 | 869.36 |
| 3.0 | 300.5 | 573.66 | 7.0 | 603.2 | 876.36 |
| 3.1 | 308.7 | 581.86 | 7.1 | 610.3 | 883.46 |
| 3.2 | 316.8 | 589.96 | 7.2 | 617.2 | 890.36 |
| 3.3 | 324.9 | 598.06 | 7.3 | 624.2 | 897.36 |
| 3.4 | 333.0 | 606.16 | 7.4 | 631.2 | 904.36 |
| 3.5 | 341.0 | 614.16 | 7.5 | 638.1 | 911.26 |
| 3.6 | 349.0 | 622.16 | 7.6 | 645.1 | 918.26 |
| 3.7 | 356.9 | 630.06 | 7.7 | 652.0 | 925.16 |
| 3.8 | 364.9 | 638.06 | 7.8 | 659.0 | 932.16 |
| 3.9 | 372.8 | 645.96 | 7.9 | 665.9 | 939.06 |
| 4.0 | 380.6 | 653.76 | 8.0 | 672.7 | 945.86 |

TABLE II (CONTD)

| DEFLECT (in.) | TEMP (°C) | TEMP (°K) | DEFLECT (in.) | TEMP (°C) | TEMP (°K) |
|------------------|--------------|--------------|------------------|--------------|--------------|
| 8.0 | 672.7 | 945.86 | 12.0 | 933.2 | 1206.36 |
| 8.1 | 679.6 | 952.76 | 12.1 | 939.4 | 1212.56 |
| 8.2 | 686.4 | 959.56 | 12.2 | 945.6 | 1218.76 |
| 8.3 | 693.2 | 966.36 | 12.3 | 951.9 | 1225.06 |
| 8.4 | 700.0 | 973.16 | 12.4 | 958.0 | 1231.16 |
| 8.5 | 706.8 | 979.96 | 12.5 | 964.1 | 1237.26 |
| 8.6 | 713.4 | 986.66 | 12.6 | 970.2 | 1243.36 |
| 8.7 | 720.2 | 993.36 | 12.7 | 976.3 | 1249.46 |
| 8.8 | 727.0 | 1000.16 | 12.8 | 982.4 | 1255.56 |
| 8.9 | 733.7 | 1006.86 | 12.9 | 988.5 | 1261.66 |
| 9.0 | 740.4 | 1013.56 | 13.0 | 994.6 | 1267.76 |
| 9.1 | 747.1 | 1020.26 | 13.1 | 1000.7 | 1273.86 |
| 9.2 | 753.7 | 1026.86 | 13.2 | 1006.8 | 1279.96 |
| 9.3 | 760.3 | 1033.46 | 13.3 | 1012.8 | 1285.96 |
| 9.4 | 766.9 | 1040.06 | 13.4 | 1018.9 | 1292.06 |
| 9.5 | 773.5 | 1046.60 | 13.5 | 1024.9 | 1298.06 |
| 9.6 | 780.1 | 1053.26 | 13.6 | 1030.8 | 1303.96 |
| 9.7 | 786.6 | 1059.76 | 13.7 | 1036.8 | 1309.96 |
| 9.8 | 793.2 | 1066.36 | 13.8 | 1042.8 | 1315.96 |
| 9.9 | 799.7 | 1072.86 | 13.9 | 1048.7 | 1321.86 |
| 10.0 | 806.2 | 1079.36 | 14.0 | 1054.6 | 1327.76 |
| 10.1 | 812.7 | 1085.86 | 14.1 | 1060.5 | 1333.66 |
| 10.2 | 819.2 | 1092.36 | 14.2 | 1066.4 | 1339.56 |
| 10.3 | 825.6 | 1098.76 | 14.3 | 1072.3 | 1345.46 |
| 10.4 | 832.1 | 1105.26 | 14.4 | 1078.2 | 1351.36 |
| 10.5 | 838.5 | 1111.66 | 14.5 | 1084.1 | 1357.26 |
| 10.6 | 844.9 | 1118.06 | 14.6 | 1089.9 | 1363.06 |
| 10.7 | 851.3 | 1124.46 | 14.7 | 1095.8 | 1368.96 |
| 10.8 | 857.7 | 1130.86 | 14.8 | 1101.7 | 1374.86 |
| 10.9 | 864.1 | 1137.26 | 14.9 | 1107.6 | 1380.76 |
| 11.0 | 870.5 | 1143.66 | 15.0 | 1113.4 | 1386.56 |
| 11.1 | 876.8 | 1149.96 | 15.1 | 1119.2 | 1392.36 |
| 11.2 | 883.1 | 1156.26 | 15.2 | 1125.1 | 1398.26 |
| 11.3 | 889.4 | 1162.56 | 15.3 | 1130.9 | 1404.06 |
| 11.4 | 895.7 | 1175.16 | 15.4 | 1136.8 | 1409.96 |
| 11.5 | 902.0 | 1181.36 | 15.5 | 1142.6 | 1415.76 |
| 11.6 | 908.2 | 1187.66 | 15.6 | 1148.4 | 1421.56 |
| 11.7 | 914.5 | 1187.66 | 15.7 | 1154.2 | 1427.36 |
| 11.8 | 920.7 | 1193.86 | 15.8 | 1160.0 | 1433.16 |
| 11.9 | 927.0 | 1200.16 | 15.9 | 1165.8 | 1438.96 |
| 12.0 | 933.2 | 1206.36 | 16.0 | 1171.5 | 1444.66 |

TABLE II (CONCLUDED)

| DEFLECT (in.) | TEMP (°C) | TEMP (°K) |
|------------------|--------------|--------------|
| 16.0 | 1171.5 | 1444.66 |
| 16.1 | 1177.3 | 1450.46 |
| 16.2 | 1183.1 | 1456.26 |
| 16.3 | 1188.9 | 1462.06 |
| 16.4 | 1194.7 | 1467.86 |
| 16.5 | 1200.5 | 1473.66 |
| 16.6 | 1206.2 | 1479.36 |
| 16.7 | 1212.0 | 1485.16 |
| 16.8 | 1217.8 | 1490.96 |
| 16.9 | 1223.5 | 1496.66 |
| 17.0 | 1229.3 | 1502.46 |
| 17.1 | 1235.1 | 1508.46 |
| 17.2 | 1240.8 | 1513.96 |
| 17.3 | 1246.6 | 1519.76 |
| 17.4 | 1252.3 | 1525.46 |
| 17.5 | 1258.1 | 1531.26 |
| 17.6 | 1263.8 | 1536.96 |
| 17.7 | 1269.6 | 1542.76 |
| 17.8 | 1275.4 | 1548.56 |
| 17.9 | 1281.1 | 1554.26 |
| 18.0 | 1286.9 | 1560.06 |
| 18.1 | 1292.6 | 1565.76 |
| 18.2 | 1298.4 | 1571.56 |
| 18.3 | 1304.1 | 1577.26 |
| 18.4 | 1309.9 | 1583.06 |
| 18.5 | 1315.7 | 1588.86 |
| 18.6 | 1321.4 | 1594.56 |
| 18.7 | 1327.2 | 1600.36 |
| 18.8 | 1333.0 | 1606.16 |
| 18.9 | 1338.7 | 1611.86 |
| 19.0 | 1344.5 | 1617.66 |
| 19.1 | 1350.3 | 1623.46 |
| 19.2 | 1356.0 | 1629.16 |
| 19.3 | 1361.8 | 1634.96 |
| 19.4 | 1367.6 | 1640.76 |
| 19.5 | 1373.4 | 1646.56 |
| 19.6 | 1379.1 | 1652.26 |
| 19.7 | 1384.9 | 1658.06 |
| 19.8 | 1390.7 | 1663.86 |
| 19.9 | 1396.4 | 1669.56 |
| 20.0 | 1402.2 | 1675.36 |

Thermogram X-axis calibration of 0.8 mv/in. deflection and a platinum, platinum 13% rhodium thermocouple with reference junctions at 0.0°C. Shenker, H., et al; "Reference Tables for Thermocouples," NBS Circular 561, April 1955, Table 3, page 13.

TABLE III
MAXRAX EMPIRICAL KINETIC PARAMETERS FOR A PHENOL FORMALDEHYDE MOLDING

| RUN NO. | 500 | 503 | 506 | 520 | 529 | 539 | LIMITING VALUES | MEAN VALUES | STANDARD DEVIATION |
|---------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|--------------------|-------------|--------------------|
| n | 1.05845 | 1.19507 | 1.13994 | 1.36876 | 1.22478 | 1.24211 | 1.21361±0.15516 | 1.20485 | 0.09522 |
| A, min ⁻¹ | 34.9036 | 73.8774 | 71.5610 | 237.429 | 88.9396 | 90.8412 | 57.2921±33.5452 | 63.9776 | 8.1150 |
| E, kcal/mole | 10.0490 | 11.1263 | 11.0672 | 12.7149 | 11.4115 | 11.4388 | 11.3820±1.3930 | 11.3013 | 0.7835 |
| r _m | 0.793167 | 0.804327 | 0.803748 | 0.819920 | 0.807209 | 0.807486 | 0.806543±0.013375 | 0.805976 | 0.000785 |
| \dot{T}_m , °C/min | 8.44 | 8.44 | 8.44 | 8.55 | 8.33 | 8.38 | 8.44±0.11 | 8.43 | 0.07 |
| T _m , °C | 532 | 532 | 532 | 527 | 532 | 532 | 530±3 | 531 | 2 |
| \dot{T}_m , °C/min | 10.13 | 10.22 | 10.32 | 10.34 | 10.00 | 9.93 | 10.13±0.20 | 10.16 | 0.15 |
| T _r , °C | 1400 | 1400 | 1400 | 1400 | 1400 | 1400 | 1400±0 | 1400 | 0 |
| w _m | 0.4589 | 0.4845 | 0.4739 | 0.5076 | 0.4888 | 0.4942 | 0.4633±0.0244 | 0.4846 | 0.0154 |
| w _r | 0.560 | 0.540 | 0.555 | 0.543 | 0.546 | 0.555 | 0.550±0.010 | 0.550 | 0.001 |
| - \dot{w}_{TM} , (°C) ⁻¹ | -0.003382 | -0.003502 | -0.003572 | -0.003702 | -0.003536 | -0.003539 | -0.003542±0.000160 | -0.003539 | 0.000095 |

TABLE IV
MAXRAX AND TRIM EMPIRICAL KINETIC PARAMETERS FOR PHENOLIC MOLDING, PHENOLIC/CARBON, AND PHENOLIC/GRAPHITE^a

| Case | RI4009 ^b (MAXRAX) | RI4009 ^b (TRIM) | RI4009 ^b (TRIM) | RI4009 ^b (TRIM) | 9-35-C ^c (MAXRAX) | 9-35-C ^c (TRIM) | 9-35-C ^c (TRIM) | 9-35-C ^c (TRIM) | 9-35-GU-1 (MAXRAX) | 9-35-GU-1 (TRIM) | 9-35-GU-1 (TRIM) | 9-35-GU-1 (TRIM) |
|--|---------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------------|---------------------|---------------------|---------------------|
| n | 1.36876 | 1 | 1.36786 | 2 | 1.01943 | 1 | 1.01943 | 2 | 1.95836 | 1 | 1.95836 | 2 |
| A, min ⁻¹ | 23.7429 | 15.5855 | 182.708 | 1782.48 | 16.8506 | 2.56923 | 2.77266 | 232.299 | 1953.91 | 11.0609 | 932.566 | 1159.62 |
| A', min ⁻¹ | | 26.9406 | 229.123 | 1920.95 | | 4.44641 | 4.75782 | 253.326 | | 20.0394 | 1020.49 | 1239.54 |
| E, kcal/mole | 12.7149 | 9.34979 | 12.3568 | 15.0580 | 9.06708 | 6.62627 | 6.70941 | 11.7983 | 15.6472 | 9.00373 | 14.3326 | 14.6013 |
| q span, °C | | 325-800 | 325-800 | 325-800 | | 325-800 | 325-800 | 325-800 | | 325-800 | 325-800 | 325-800 |
| r _m | 0.819920 | | | | 0.782113 | | | | 0.844740 | | | |
| Ṫ, °C/min | 8.55 | | | | 8.28 | | | | 8.28 | | | |
| T _m , °C | 527 | | | | 532 | | | | 516 | | | |
| Ṫ _m , °C/min | 10.34 | | | | 10.22 | | | | 10.00 | | | |
| T _r , °C | 1400 | | | | 1400 | | | | 1400 | | | |
| w _m | 0.5076 | | | | 0.4455 | | | | 0.5730 | | | |
| w _r | 0.543 | | | | 0.916 | | | | 0.843 | | | |
| -ẇ _{Tm} , (°C) ⁻¹ | -0.003702 | | | | -0.003076 | | | | -0.003695 | | | |

^ar_m, Ṫ, T_r, w_r values under MAXRAX used for TRIM. MAXRAX n used for one TRIM run; two additional n's were assumed for TRIM

^bRun No. 520

^cAverage values using the second step of two major reactions

TABLE V
EMPIRICAL KINETIC PARAMETERS FOR PHENOL FORMALDEHYDE MOLDING:
THREE HEATING RATES, SIX REPLICATE RUNS, AND A SURVEY

| CASE | THREE HEATING RATES (Via PRIM) | | | | SIX REPLICATE RUNS (Via MAXRAX) | | | | MATERIALS SURVEY (Via PRIM) | | | |
|--|--------------------------------|------------|--------------------|--------------------|---------------------------------|--------------------|-------------------|------------|-----------------------------|------------|--------------------|--|
| | Limiting Values | Mean Value | Standard Deviation | Limiting Values | Mean Value | Standard Deviation | Limiting Values | Mean Value | Limiting Values | Mean Value | Standard Deviation | |
| n | 1.47624±0.00954 | 1.47481 | 0.00794 | 1.21361±0.15516 | 1.20485 | 0.09522 | 1.55578±0.07002 | 1.53886 | 1.55578±0.07002 | 1.53886 | 0.06657 | |
| A, min ⁻¹ | 60.9338±41.2902 | 63.9156 | 34.0500 | 57.2921±33.5492 | 63.9976 | 8.1150 | 60.9338±41.3902 | 49.5834 | 60.9338±41.3902 | 49.5834 | 9.2430 | |
| E, kcal/mole | 10.8559±0.7226 | 10.9926 | 0.1963 | 11.3820±1.3330 | 11.3013 | 0.7835 | 10.3803±1.1983 | 10.6044 | 10.3803±1.1983 | 10.6044 | 0.8102 | |
| r _m | 0.792511±0.011756 | 0.793094 | 0.009634 | 0.806543±0.013376 | 0.805976 | 0.000785 | 0.792490±0.011736 | 0.793344 | 0.792490±0.011736 | 0.793344 | 0.008896 | |
| Ṫ, °C/min | 4.97±2.42 | 5.00 | 1.98 | 8.44±0.11 | 8.43 | 0.07 | 5.12±2.58 | 5.16 | 5.12±2.58 | 5.16 | 1.88 | |
| T _m , °C | 500±10 | 510 | 8 | 530±3 | 531 | 2 | 882±68 | | 882±68 | | | |
| Ṫ _m , °C/min | 4.97±2.42 | 5.00 | 1.98 | 10.13±0.20 | 10.16 | 0.15 | | | | | | |
| T _r , °C | 950±0 | 950 | 0 | 1400±0 | 1400 | 0 | 882±68 | 928 | 882±68 | 928 | 8 | |
| w _m | | | | 0.4833±0.0244 | 0.4846 | 0.0154 | | | | | | |
| w _r | 0.554±0.002 | 0.553 | 0.002 | 0.550±0.010 | 0.550 | 0.001 | 0.577±0.025 | 0.561 | 0.577±0.025 | 0.561 | 0.018 | |
| -ẇ _{Tm} , (°C) ⁻¹ | | | | -0.003542±0.000160 | -0.003539 | 0.000095 | | | | | | |

TABLE VI
MAXRAX EMPIRICAL KINETIC PARAMETERS
FOR PHENOLIC/CARBON MULTIPLE-STEP REACTIONS

| CASE | 9-35-C First Step | 9-35-C Second Step | 9-35-C Average |
|---------------------------------------|----------------------|--------------------------|-------------------|
| n | 1.00000 | 7.26559 | 1.01943 |
| A, min ⁻¹ | 264174 | 5.15116x10 ¹⁶ | 16.8506 |
| E, kcal/mole | 19.8712 | 63.3838 | 9.06708 |
| r _m | 0.882126 | 0.953570 | 0.782113 |
| \dot{T} , °C/min | 8.28 | 8.28 | 8.28 |
| T _m , °C | 428 | 532 | 532 |
| \dot{T} _m , °C/min | 10.06 | 10.22 | 10.22 |
| T _r , °C | 480 | 1400 | 1400 |
| w _m | 0.342 | 0.759 | 0.446 |
| w _r | 0.924 | 0.816 | 0.816 |
| $-\dot{w}_{T_m}$, (°C) ⁻¹ | -0.006960 | -0.005140 | -0.003080 |

TABLE VII
FINAL RESIDUAL WEIGHT FRACTIONS

| CASE | RI4009 | | | | | | | | |
|------------------------------------|--------|-------|-------|-------|-------|-------|--------|-----------|--|
| Run No. | 500 | 503 | 506 | 520 | 529 | 539 | 9-35-C | 9-35-GU-1 | |
| Sample Residual Weight Fraction | | | | | | | | | |
| Analytical Balance | 0.538 | 0.547 | 0.535 | 0.542 | 0.535 | 0.545 | 0.806 | 0.841 | |
| Thermogram | 0.560 | 0.540 | 0.555 | 0.543 | 0.546 | 0.555 | 0.816 | 0.843 | |
| Resin Residual Weight Fraction* | | | | | | | | | |
| Analytical Balance | | | | | | | 0.721 | 0.590 | |
| Thermogram | | | | | | | 0.694 | 0.651 | |

*Estimated values assuming residual weights of 0.874 for carbon cloth and 0.987 for graphite cloth.

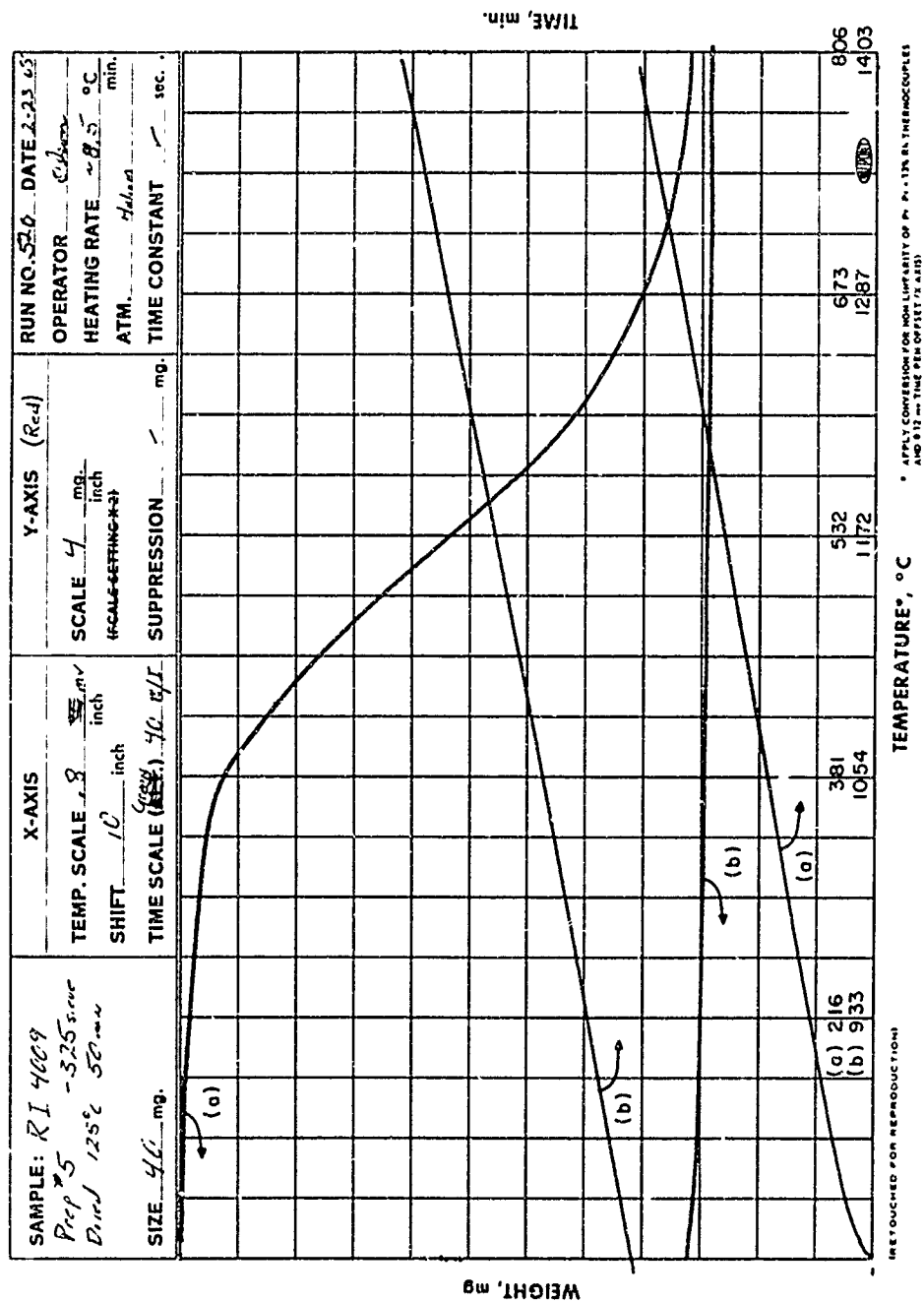


Figure 1. Thermogram of Phenol Formaldehyde Molding (RI4009)

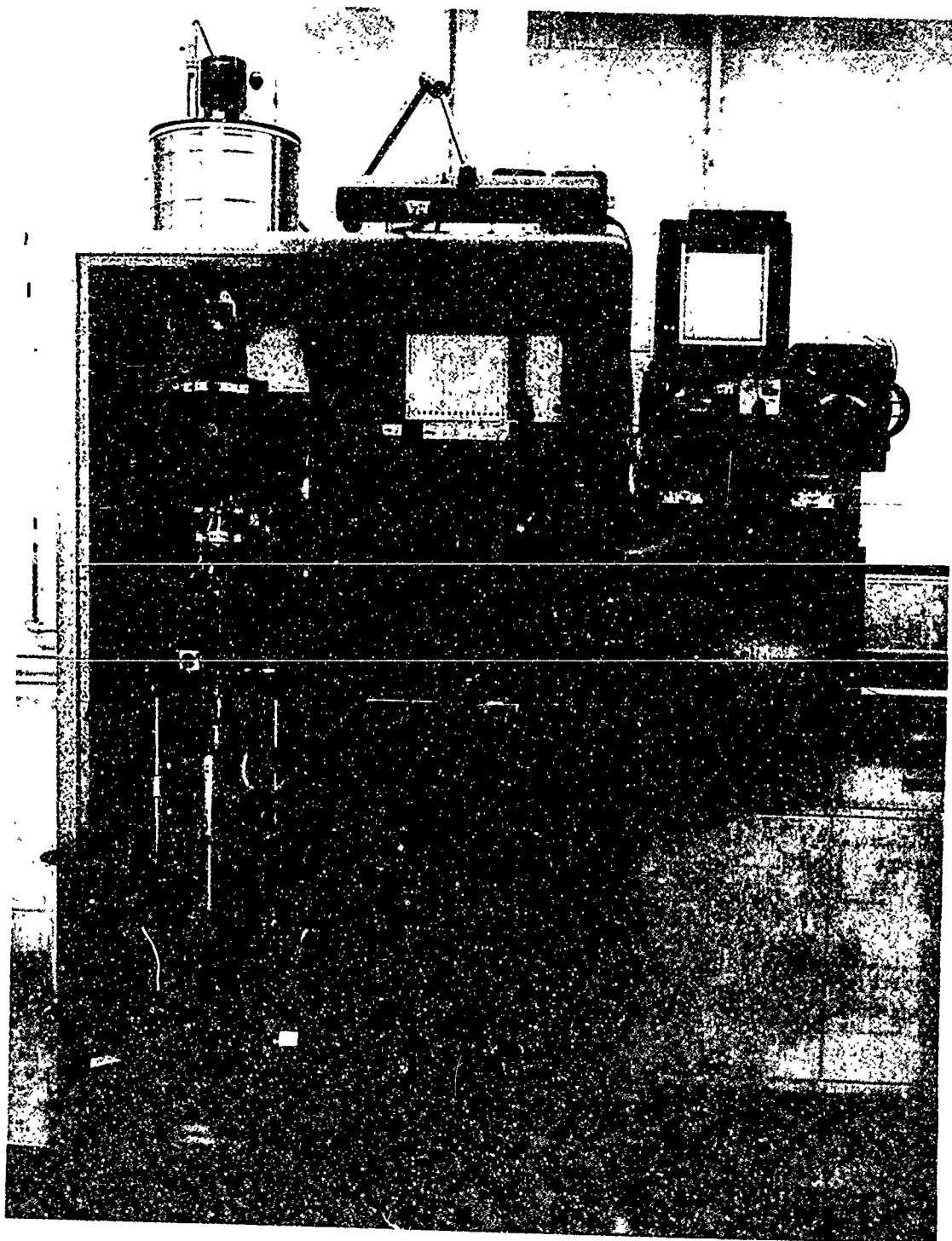


Figure 2. General View of the Recording Thermobalance

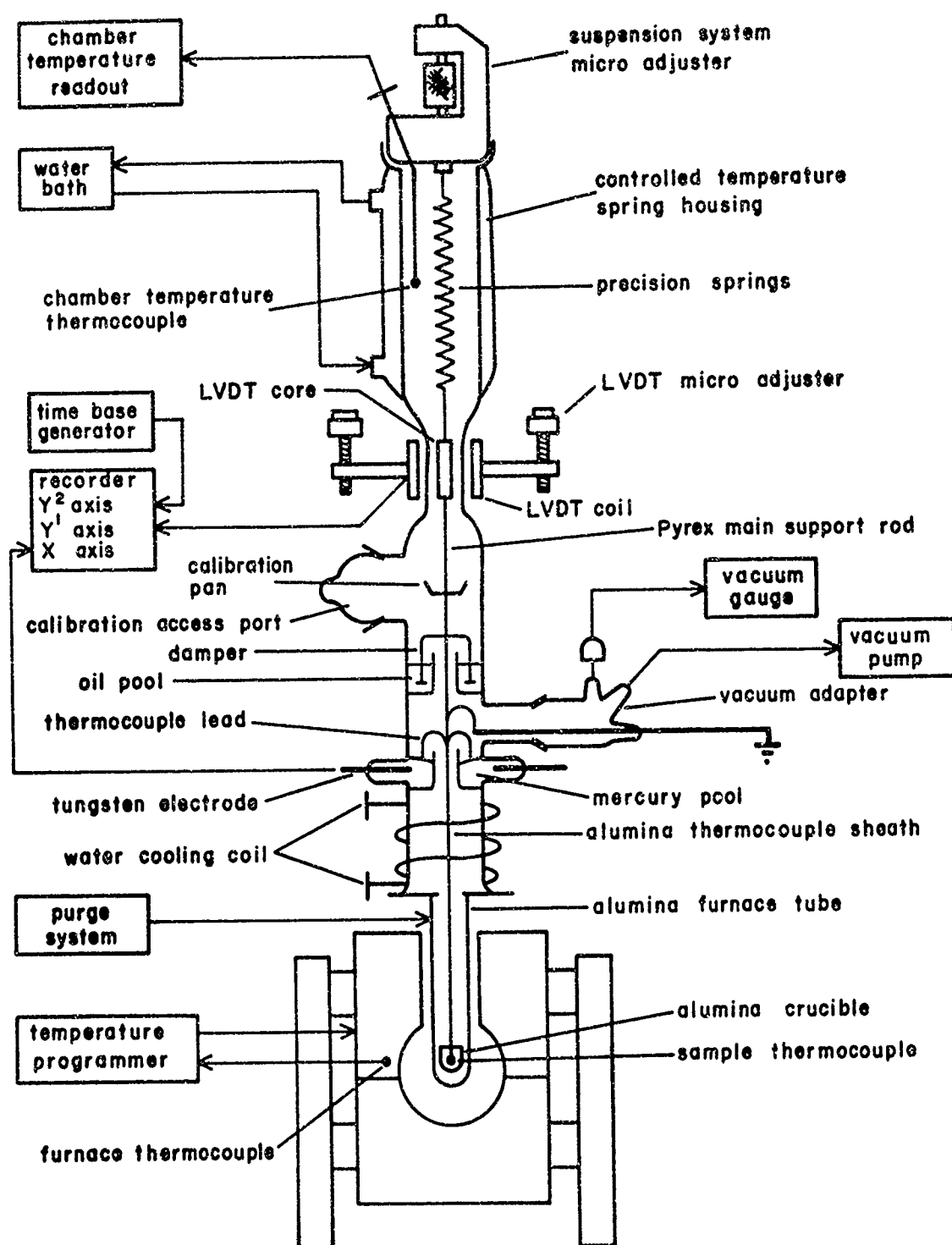


Figure 3. Functional View of the Recording Thermobalance

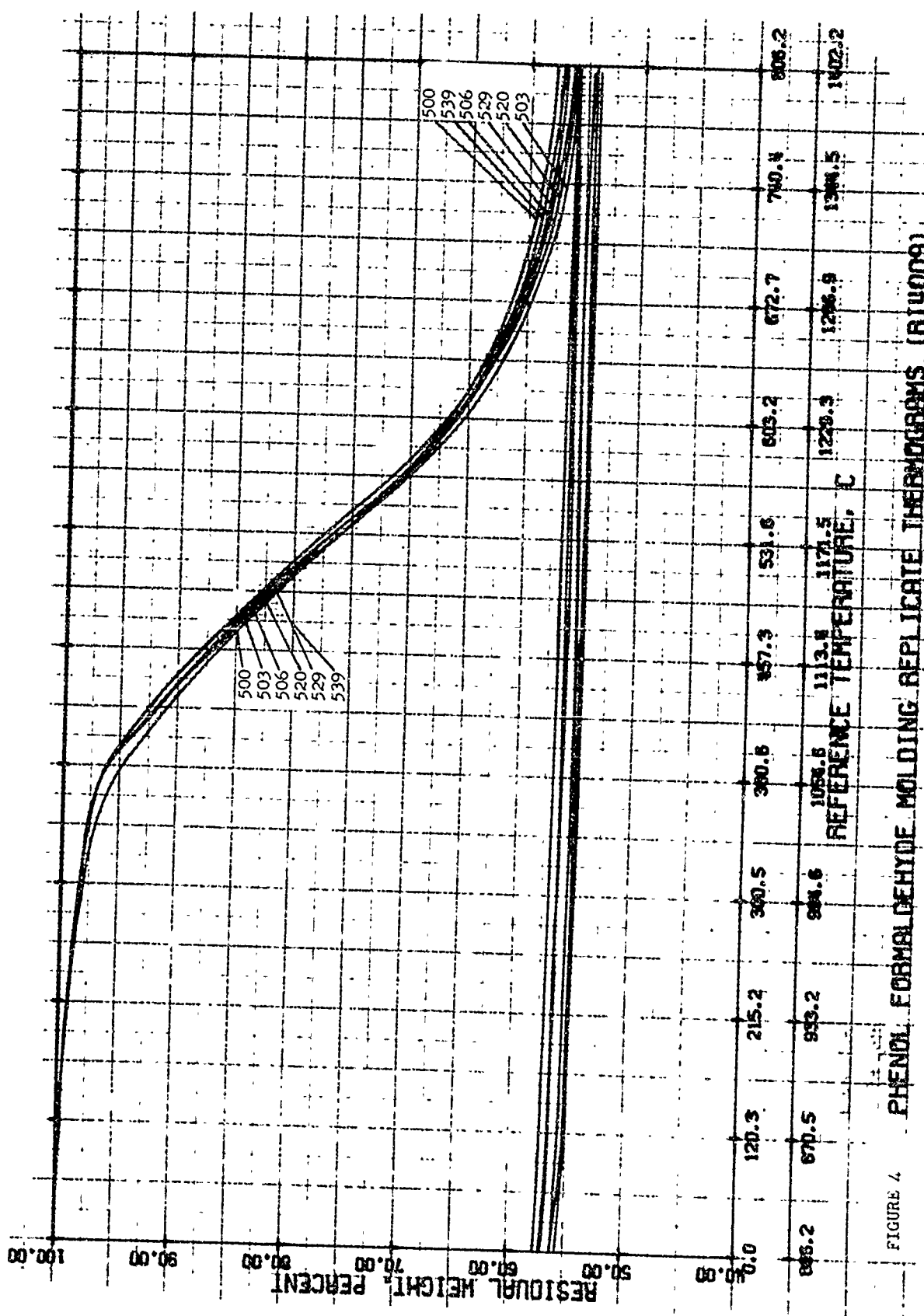
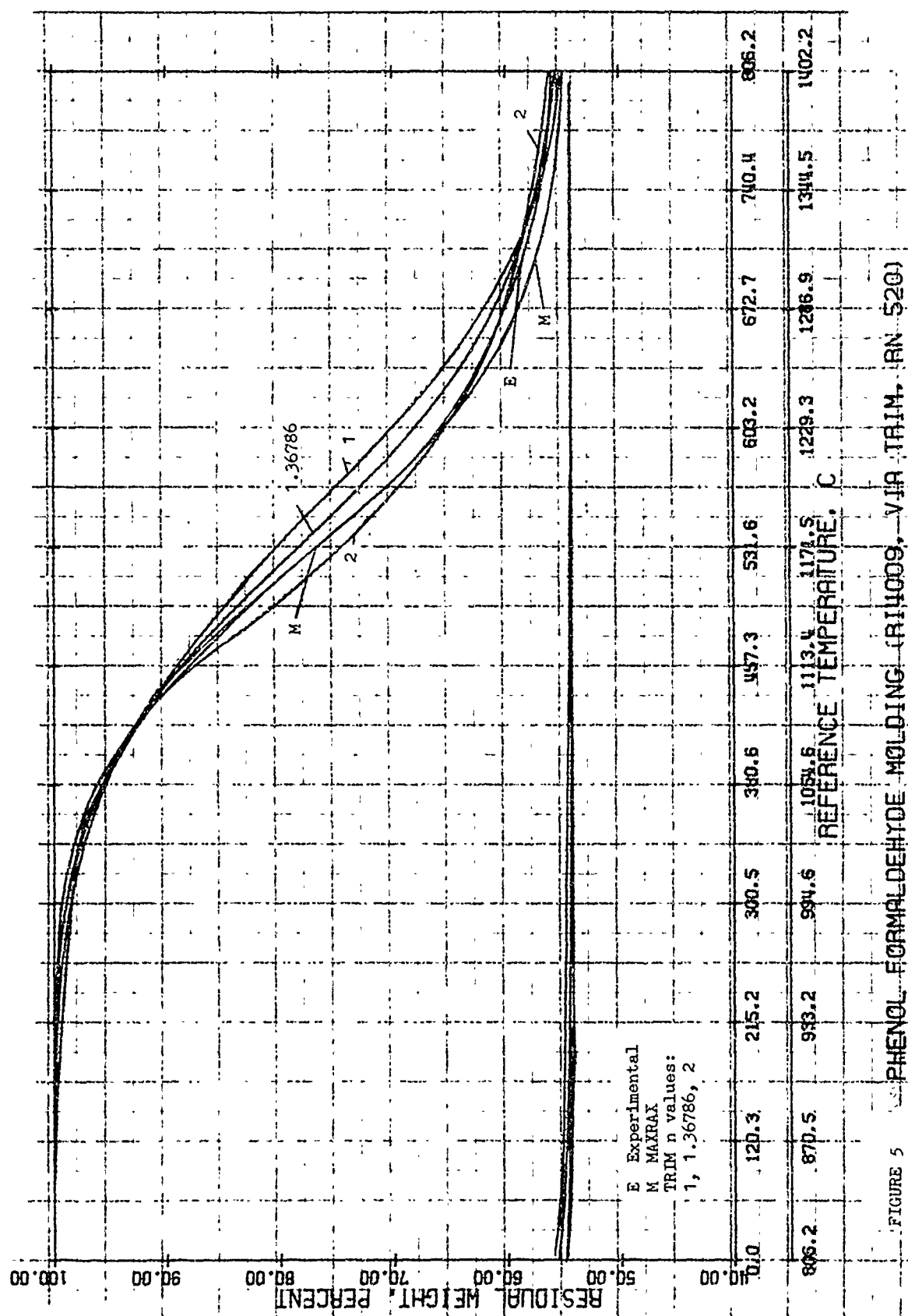
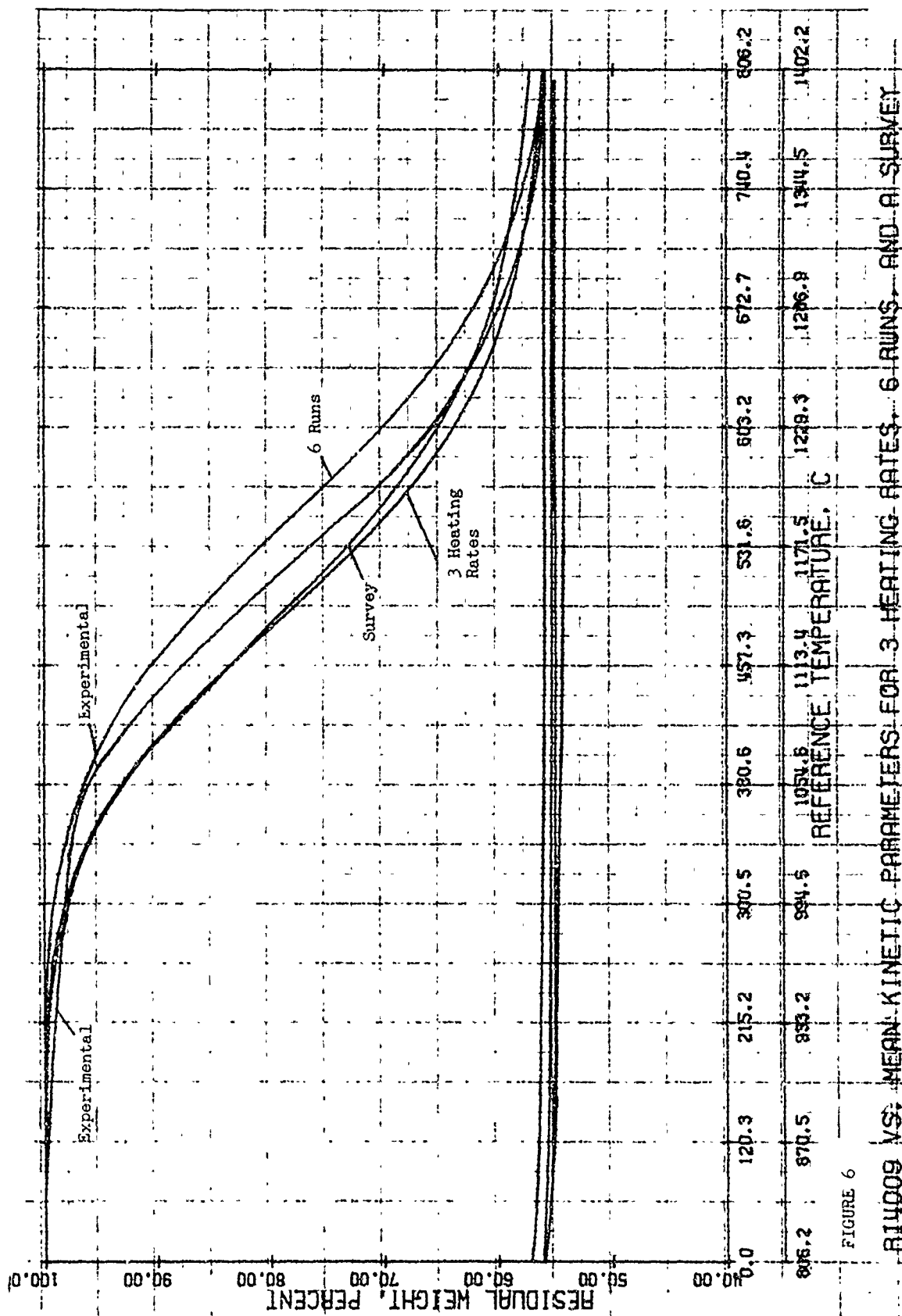


FIGURE 4 PHENOL FORMALDEHYDE MOLDING REPLICATE THERMOGRAMS (R14009)





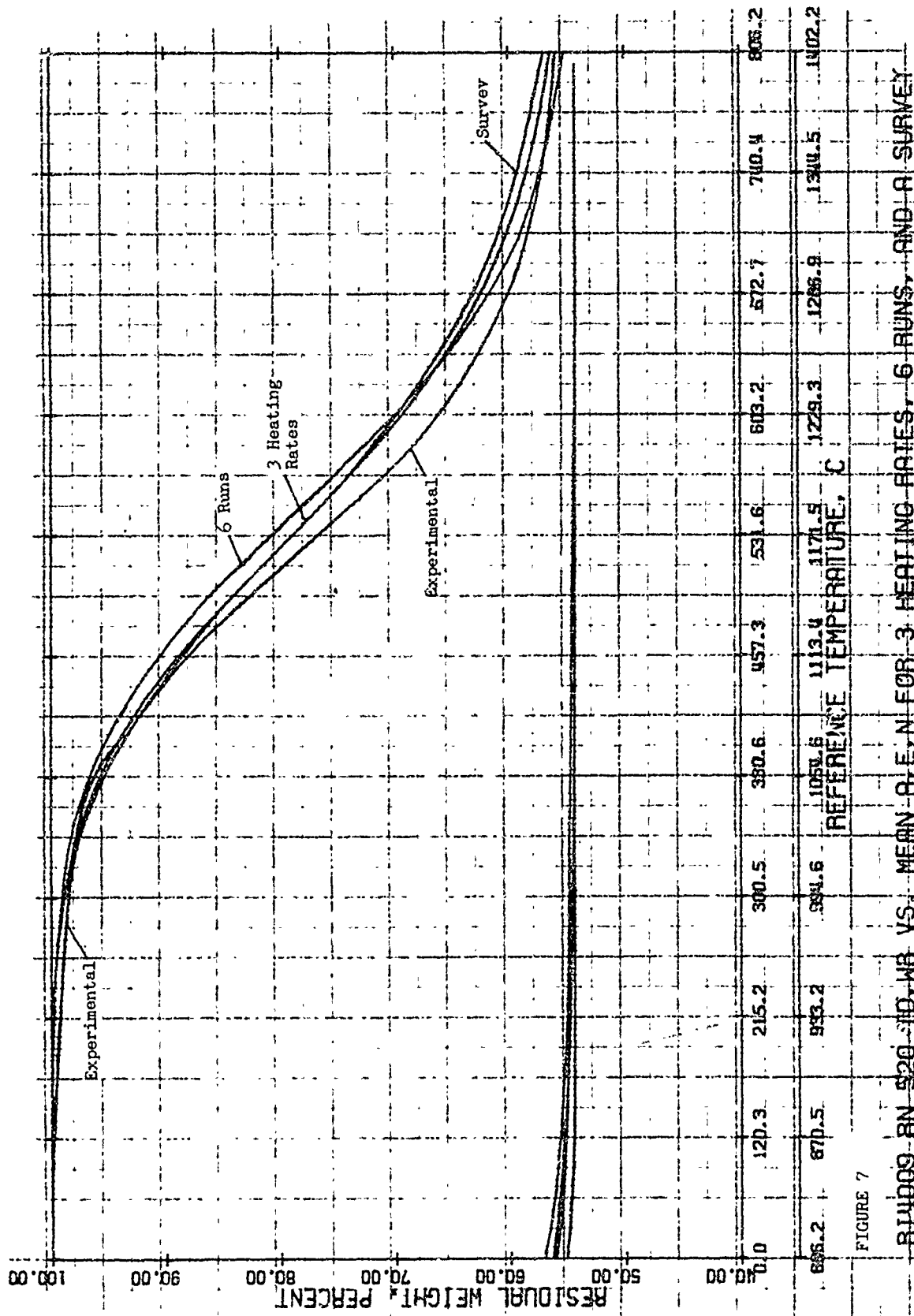
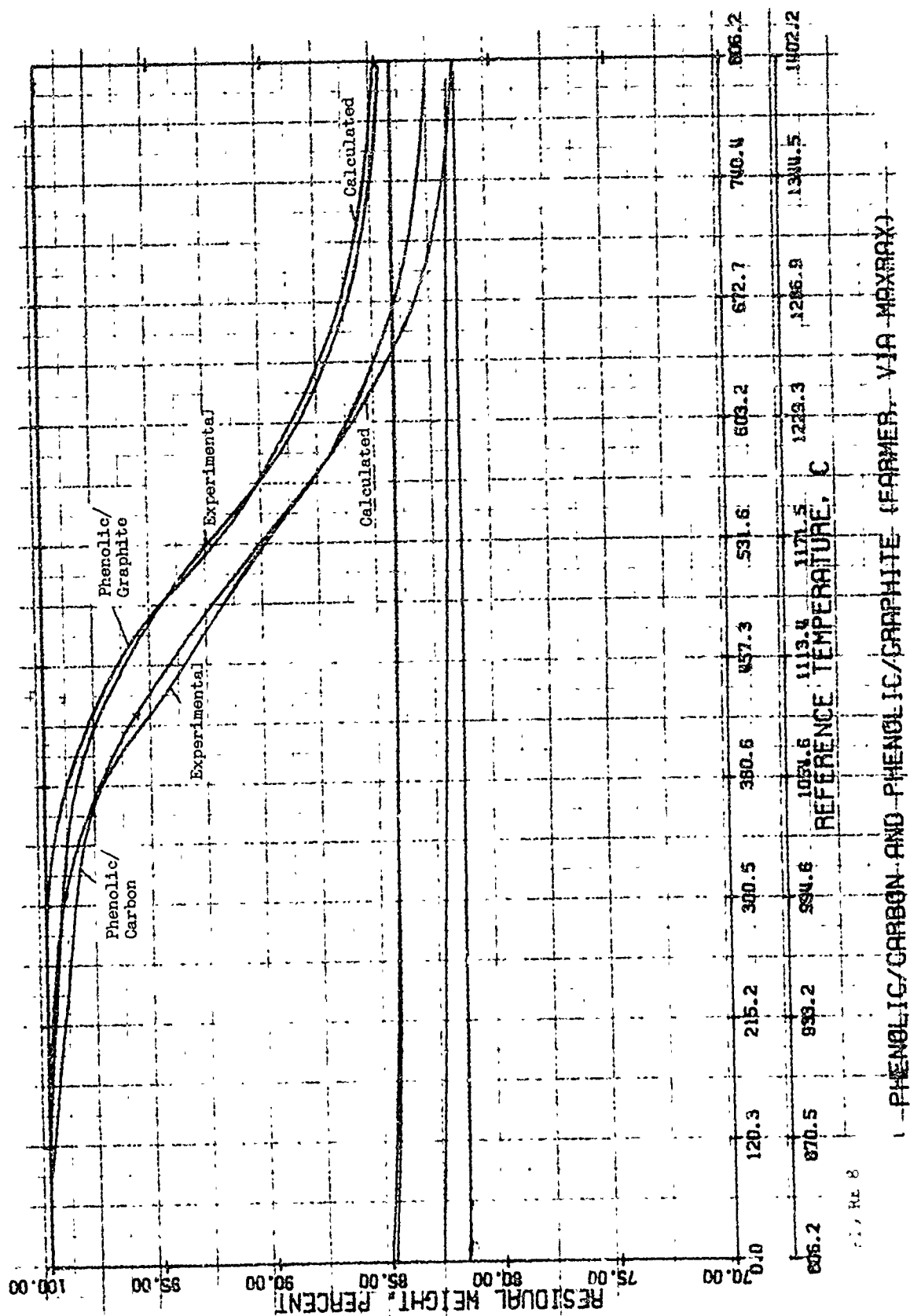


FIGURE 7

R14009 RN 520-110-WR VS. MEAN RATE FOR 3 HEATING RATES, 6 RUNS, AND A SURVEY



PHENOLIC/CARBON AND PHENOLIC/GRAPHITE (FARMER, VIA MAXBAX)

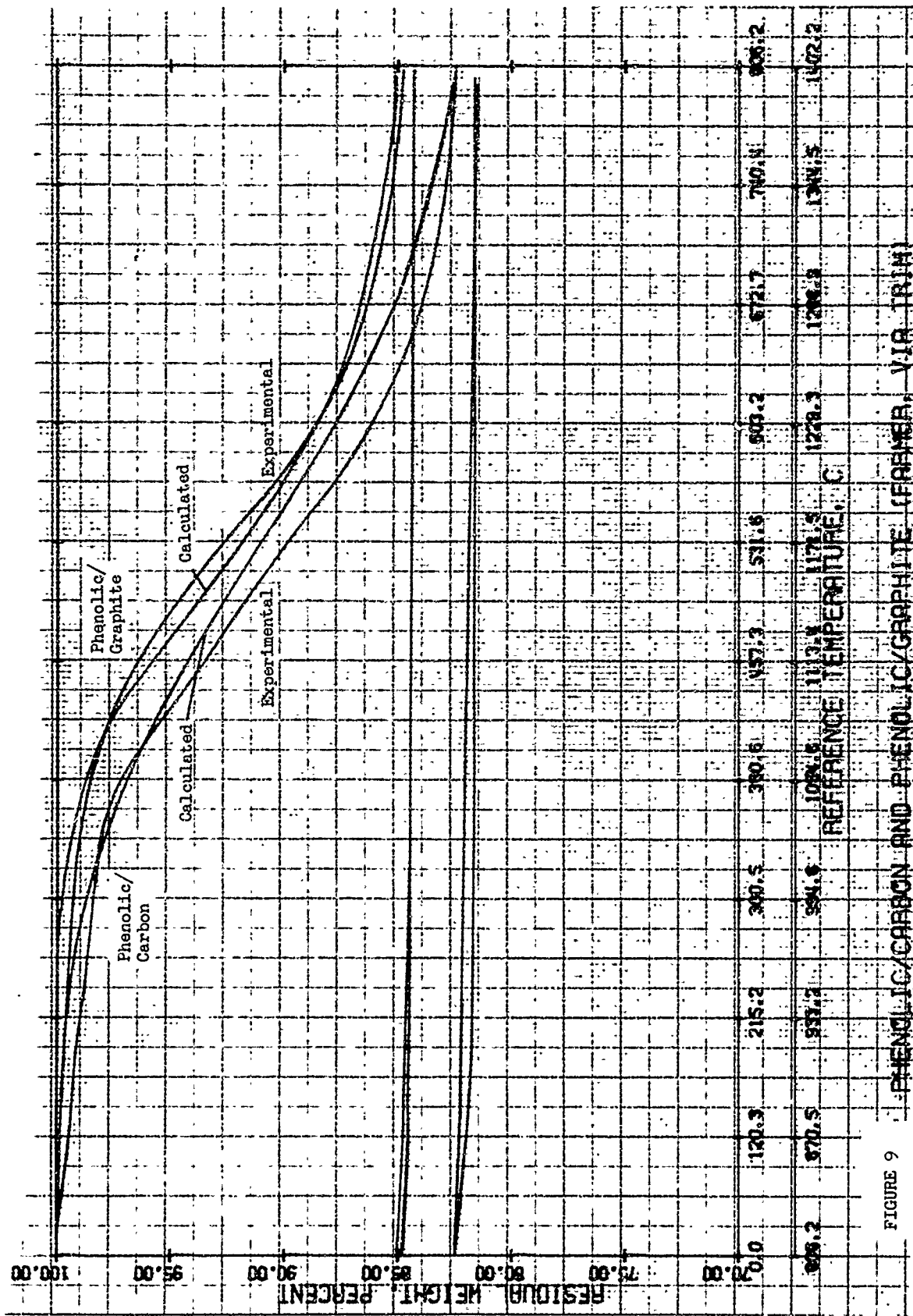
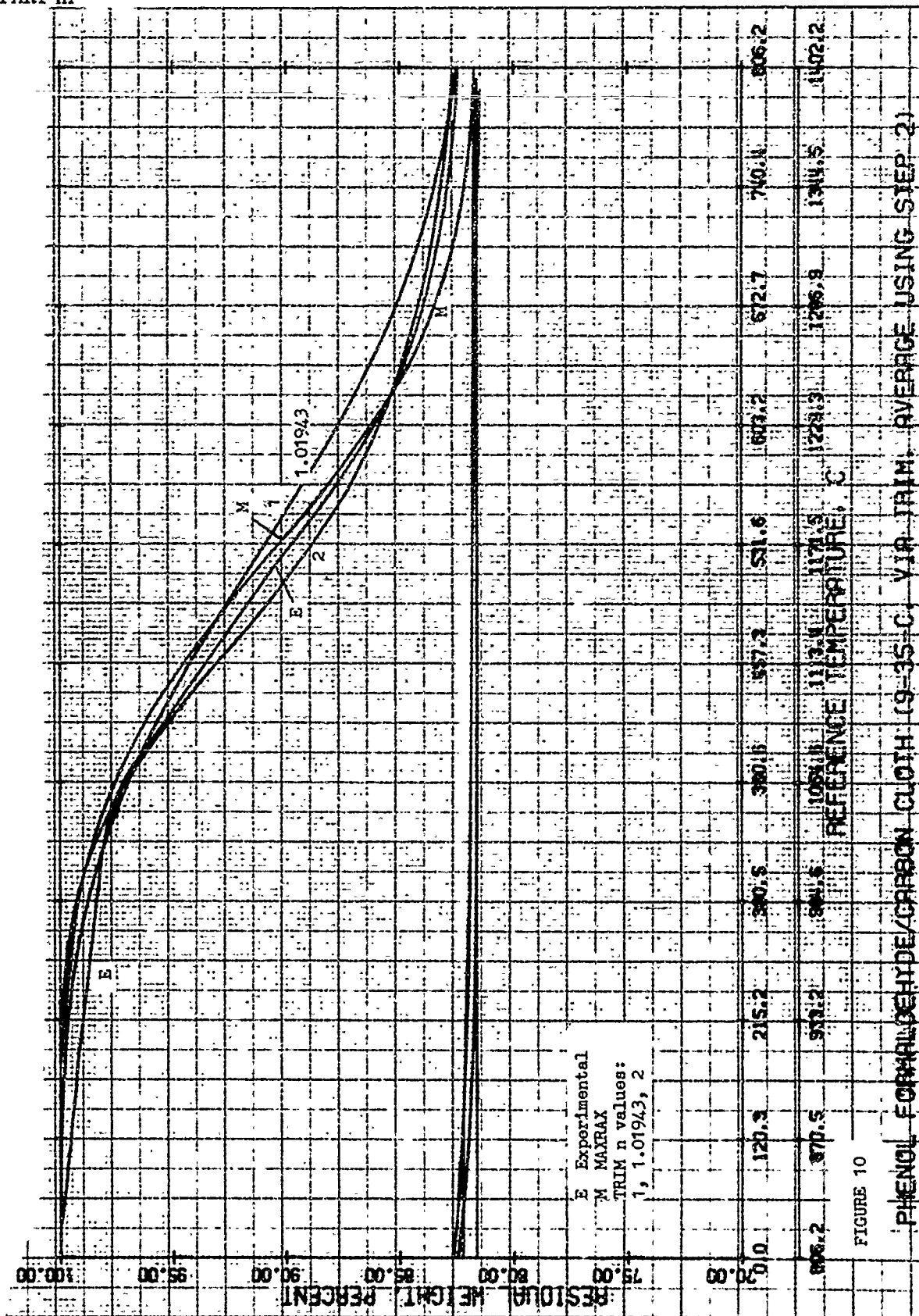
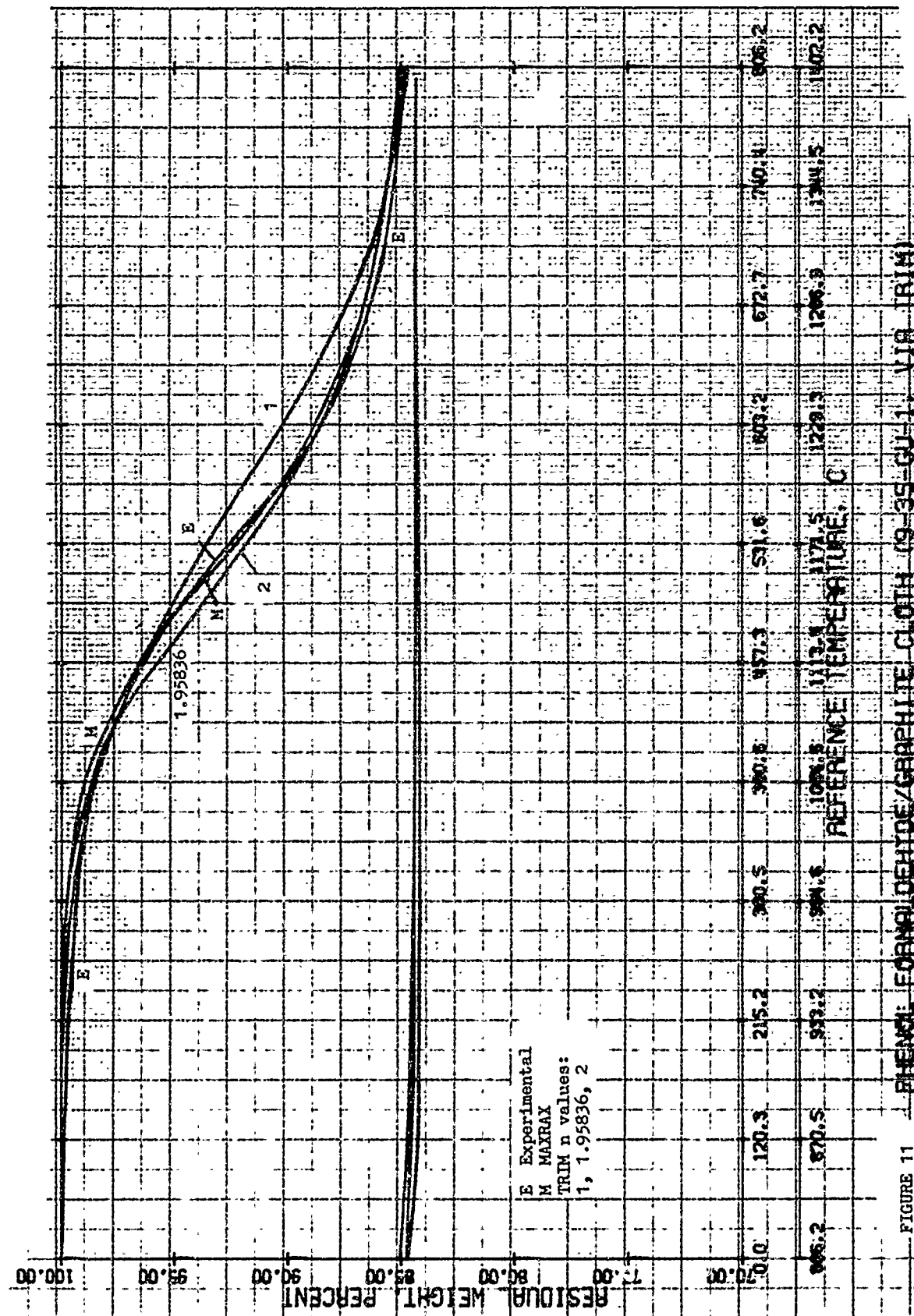


FIGURE 9 PHENOLIC/CARBON AND PHENOLIC/GRAPHITE (FARNER, VIA TRIM)





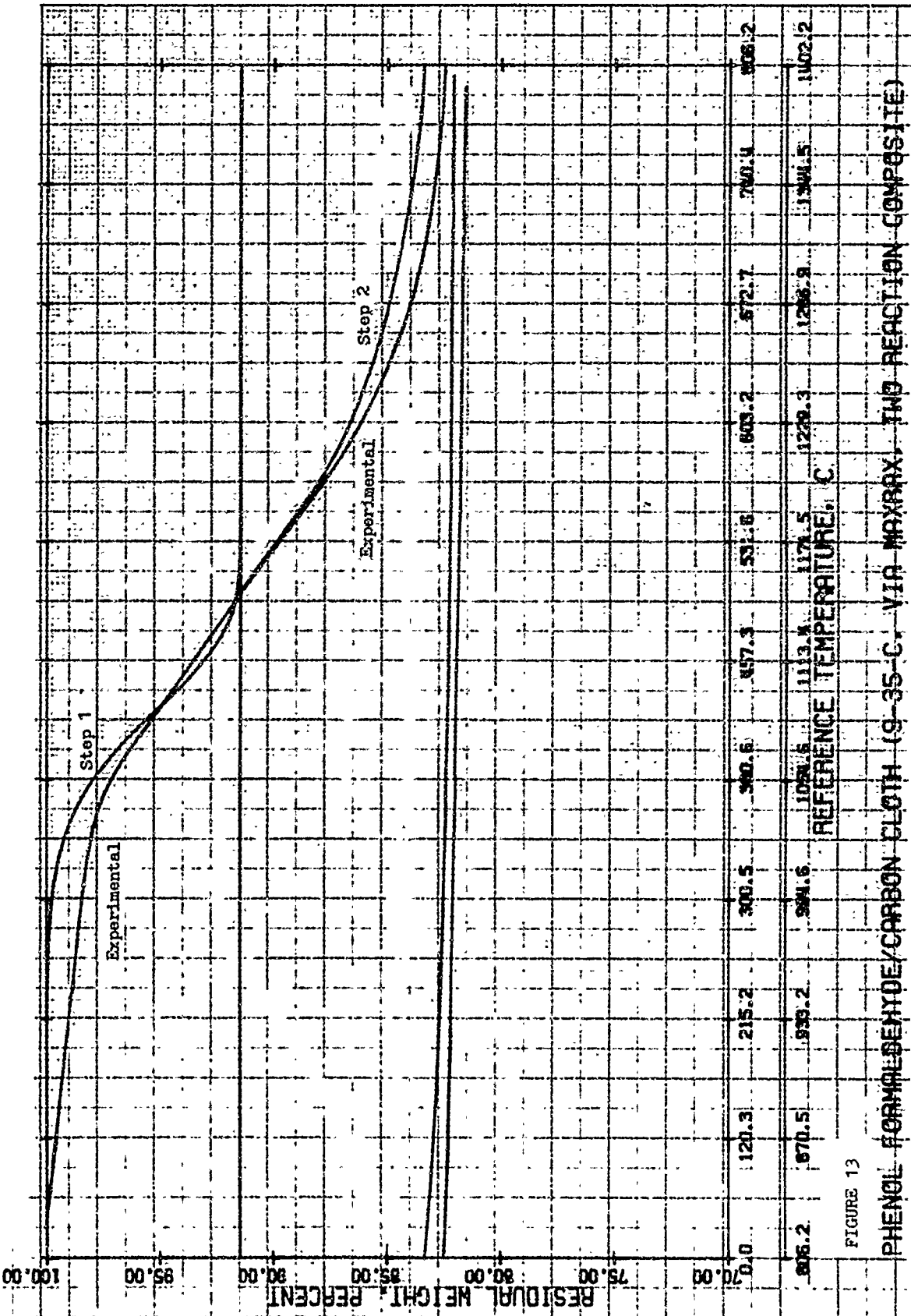
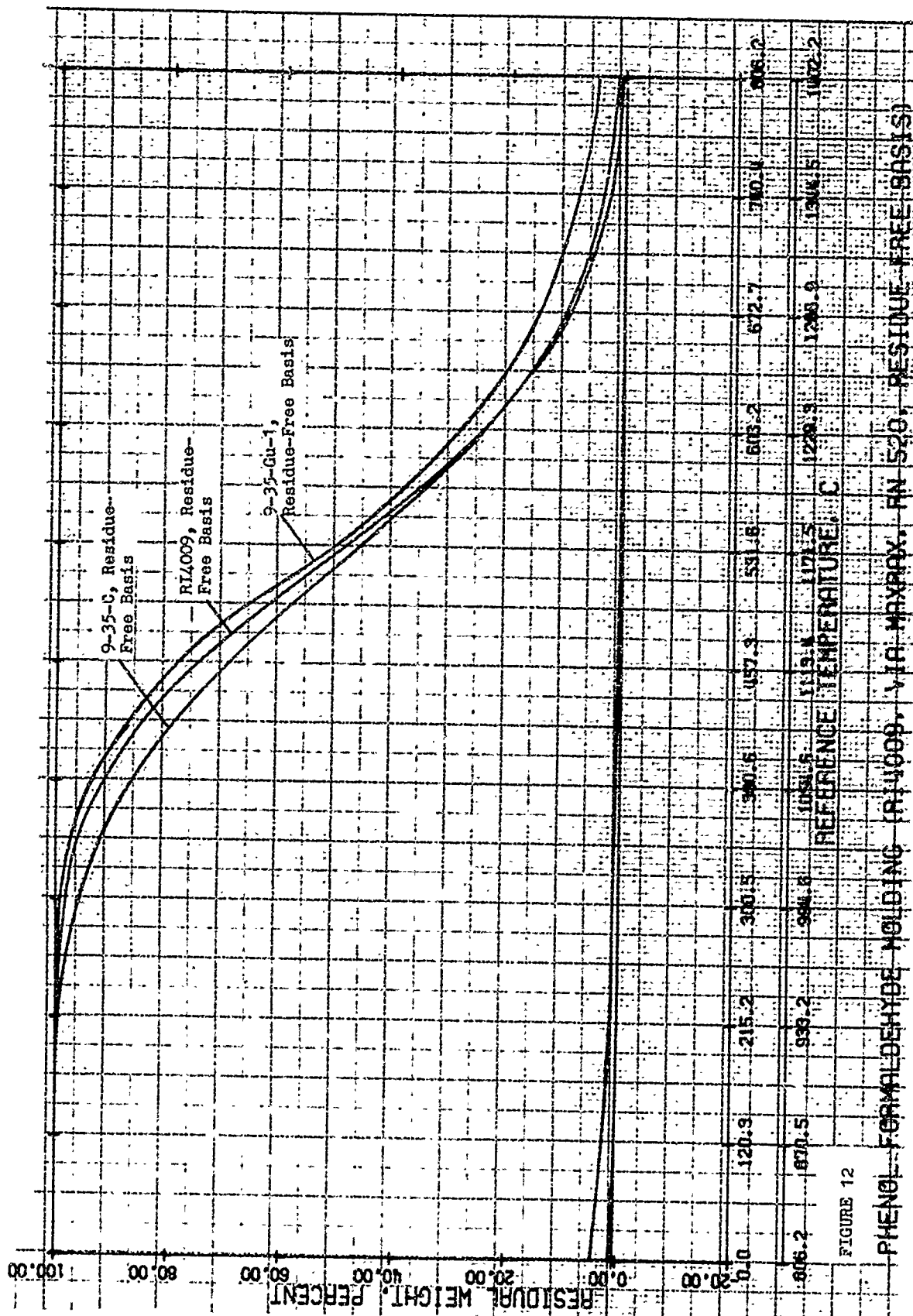
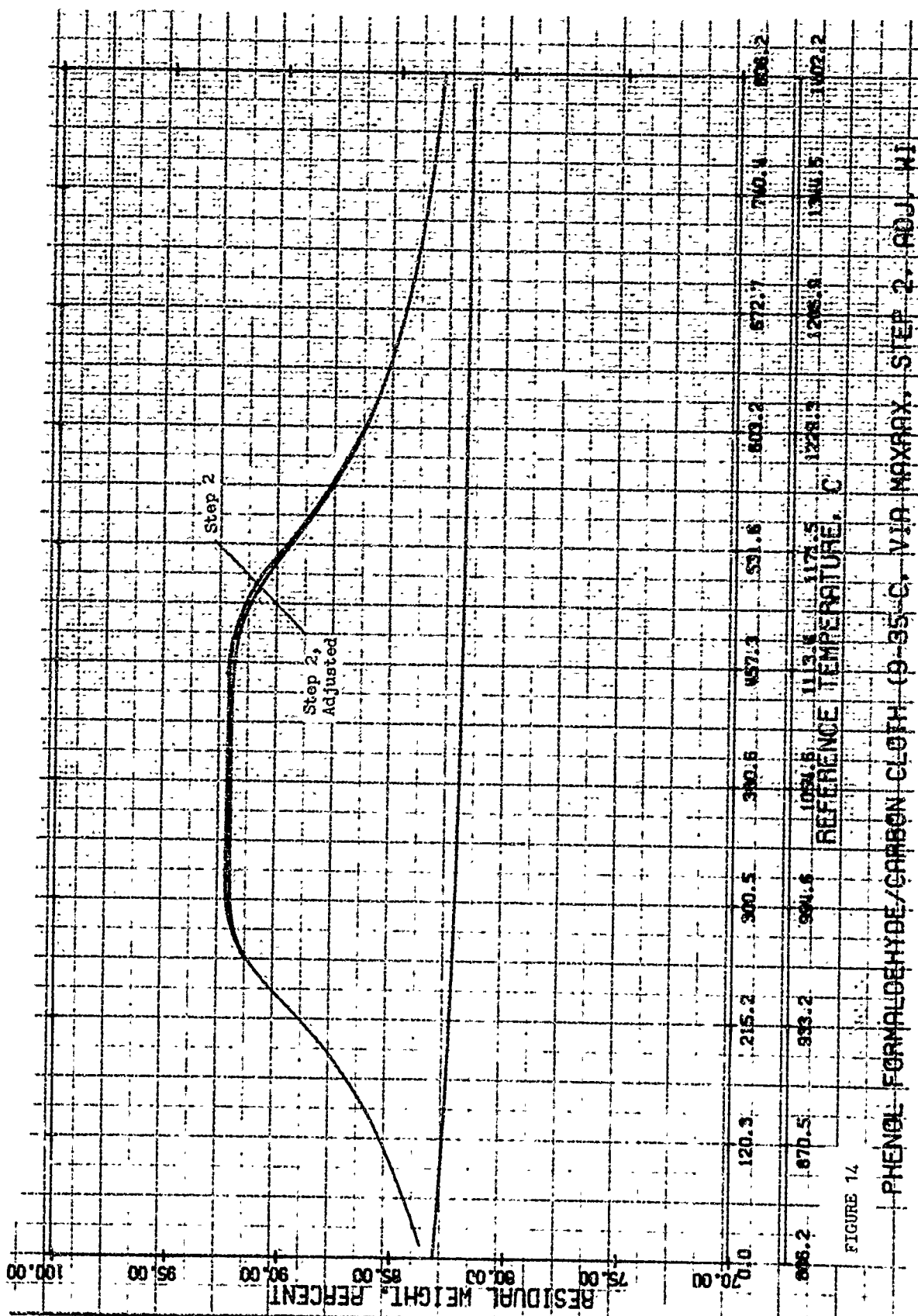


FIGURE 13

PHENOLIC FORMALDEHYDE/CARBON CLOTH (9-35-C, V1A MAXRAX, TWO REACTION COMPOSITE)





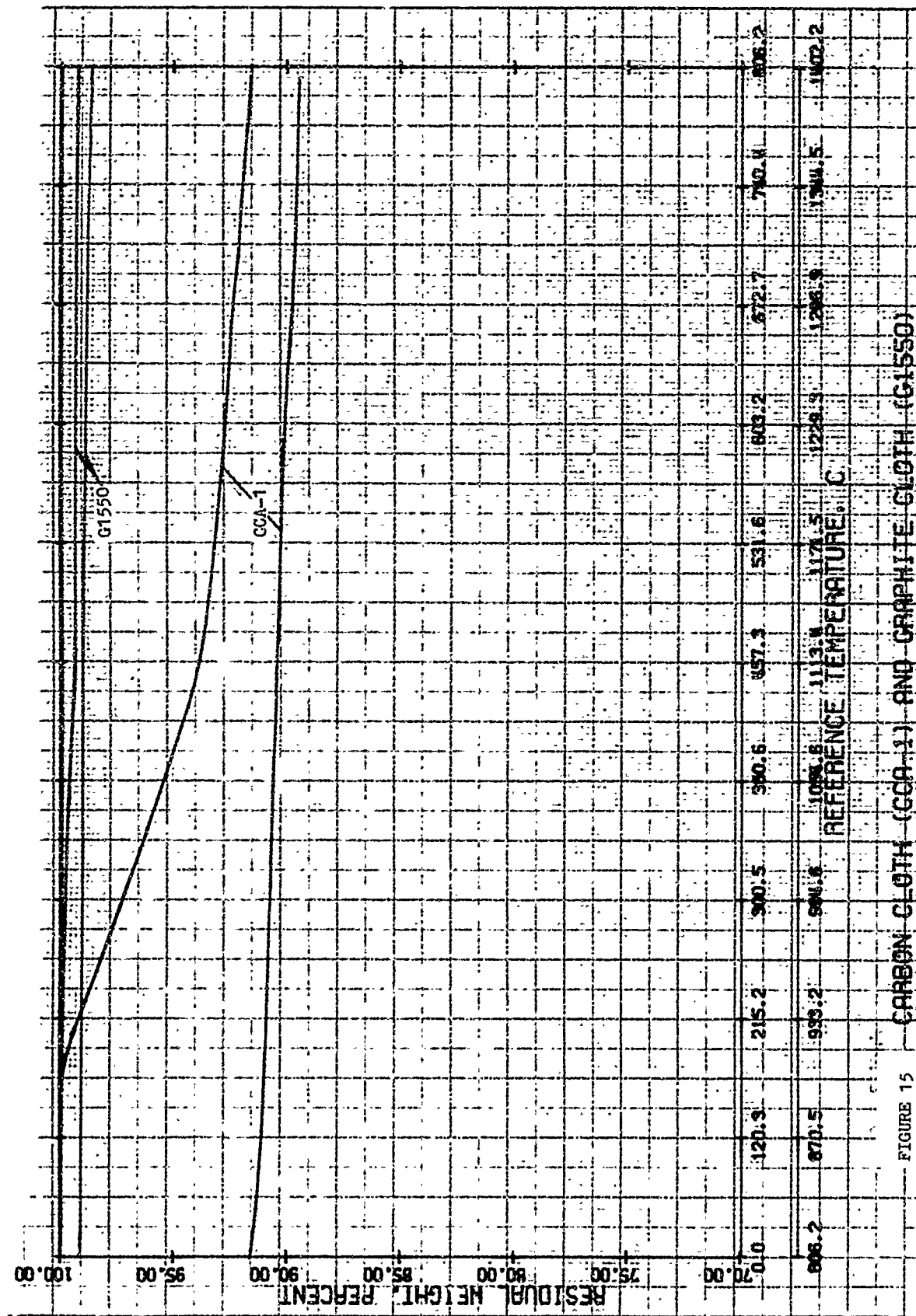
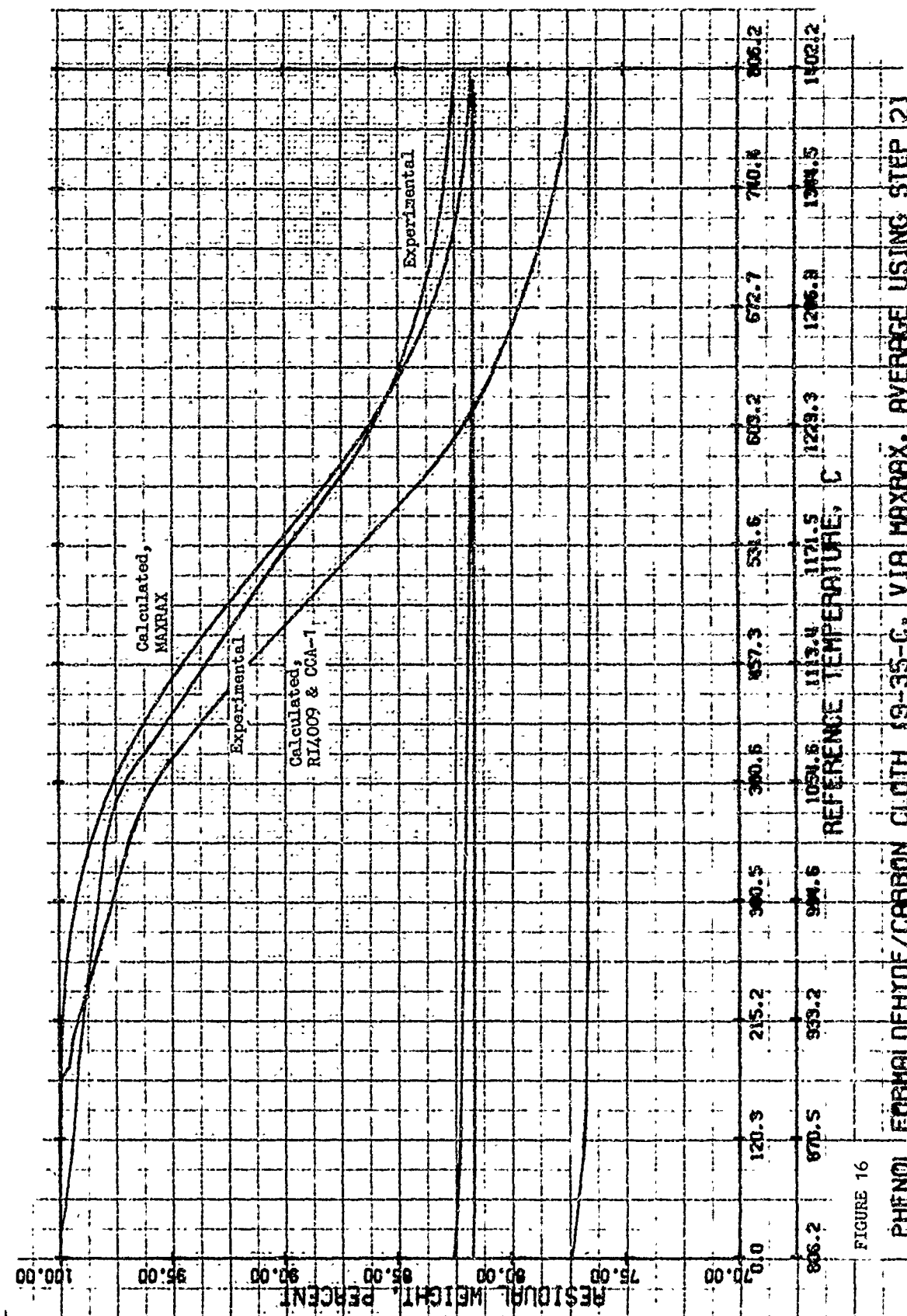


FIGURE 15 CARBON CLOTH (CCA-1) AND GRAPHITE CLOTH (G1550)



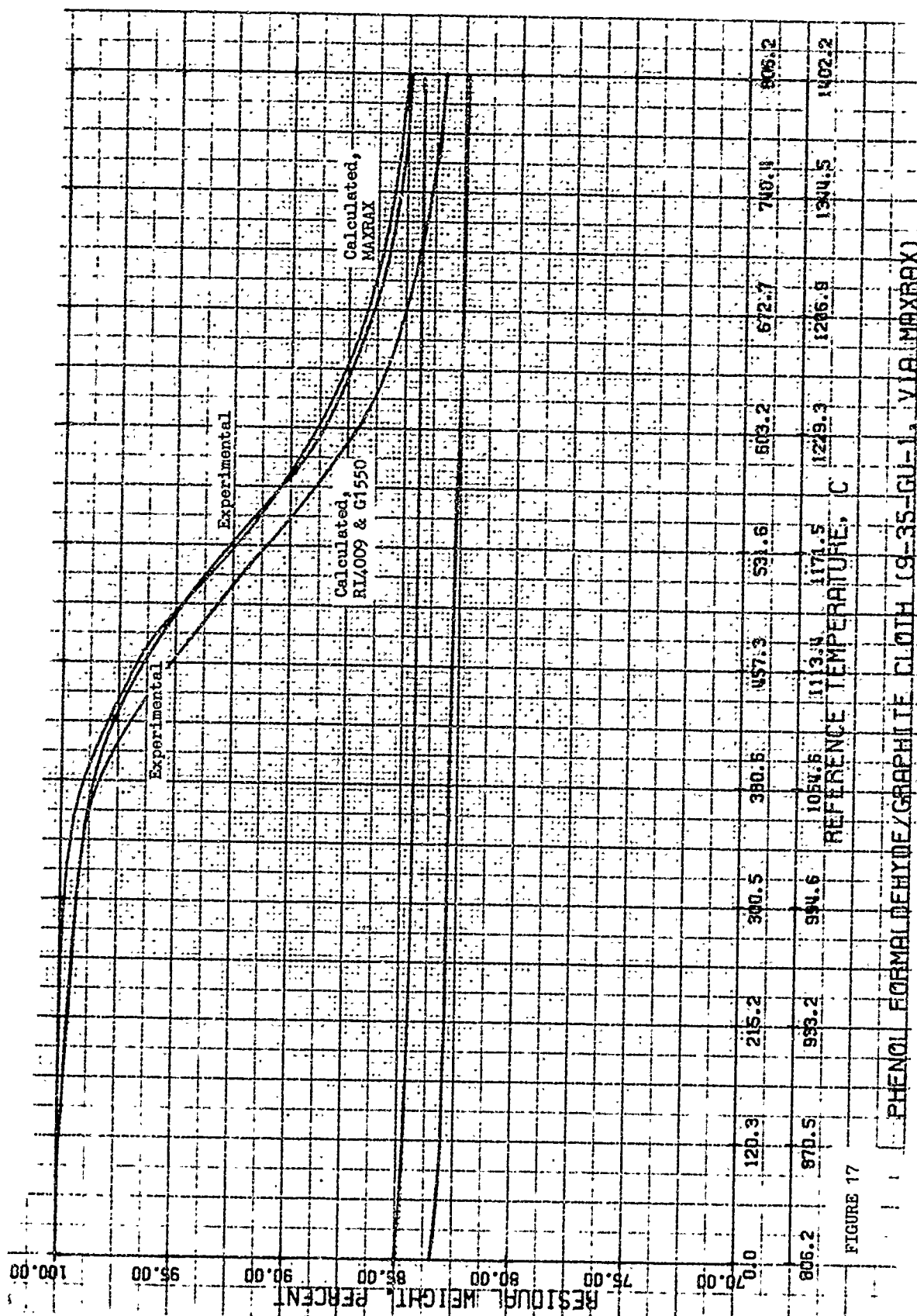


FIGURE 17

PHENOL FORMALDEHYDE/GRAPHITE CLOTH (9-35-GU-1, VIA MAXRAX)

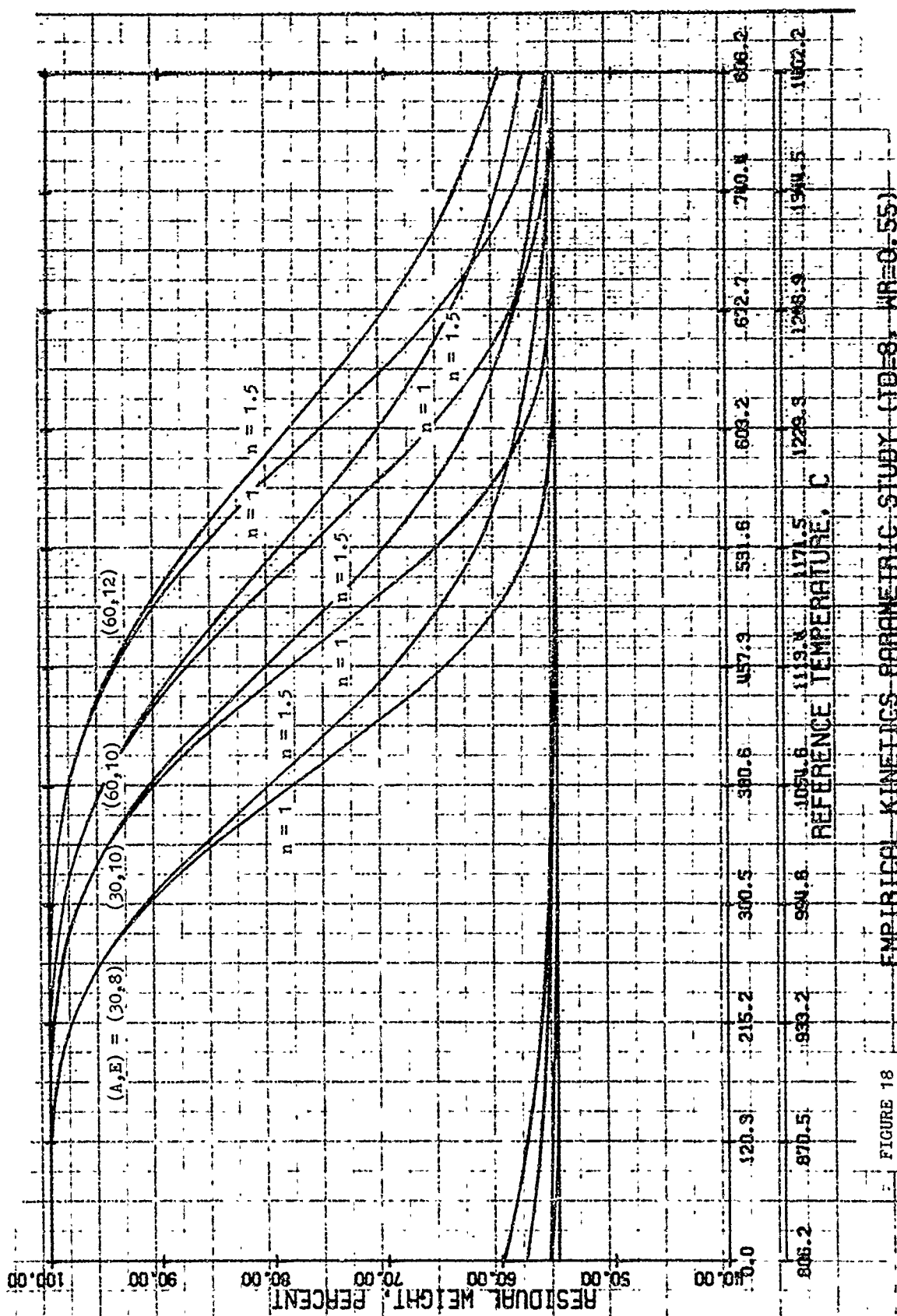


FIGURE 18 EMPIRICAL KINETICS PARAMETRIC STUDY (ID=81, WR=0.55)

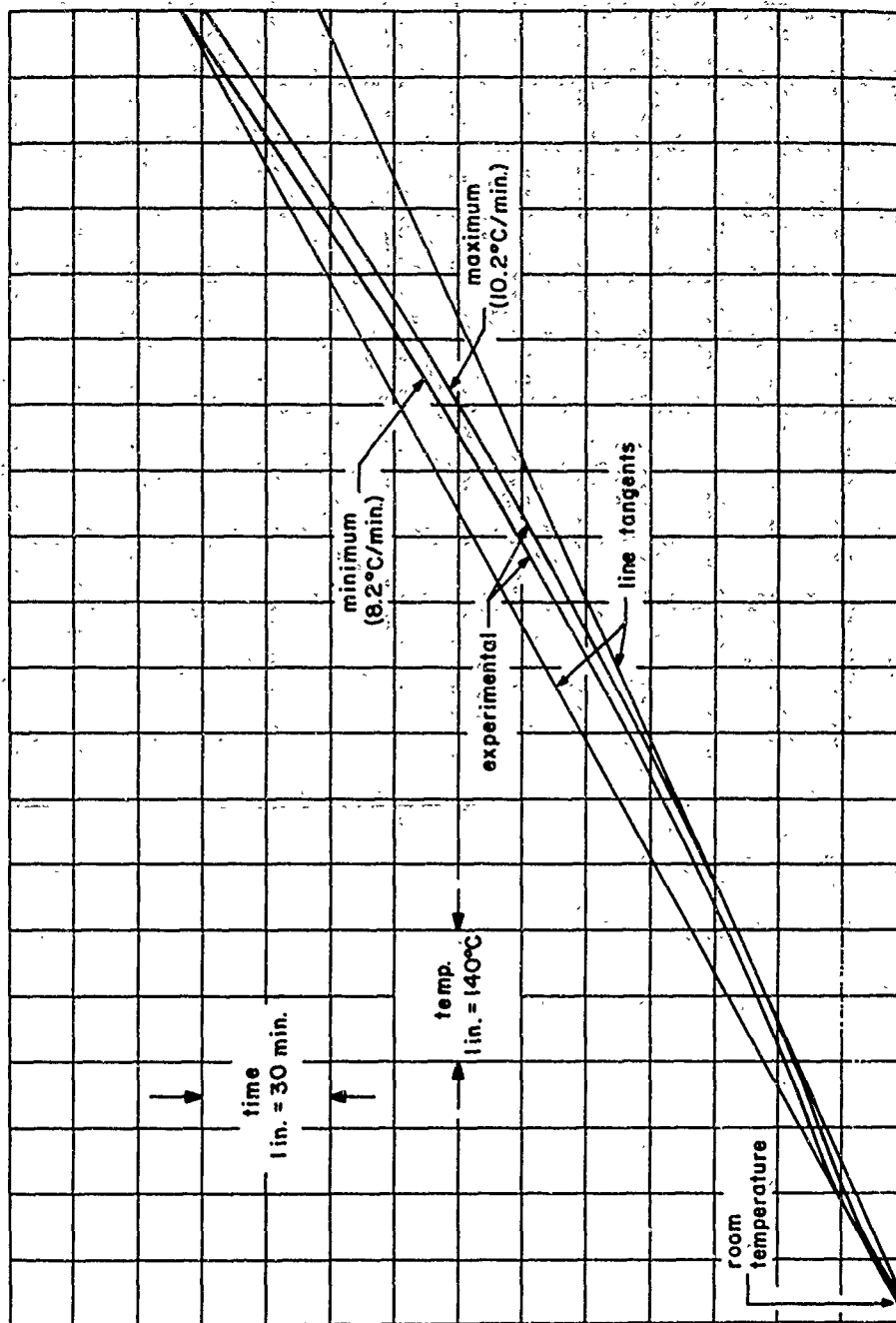


Figure 19. Heating Rate Linearity and Reproducibility

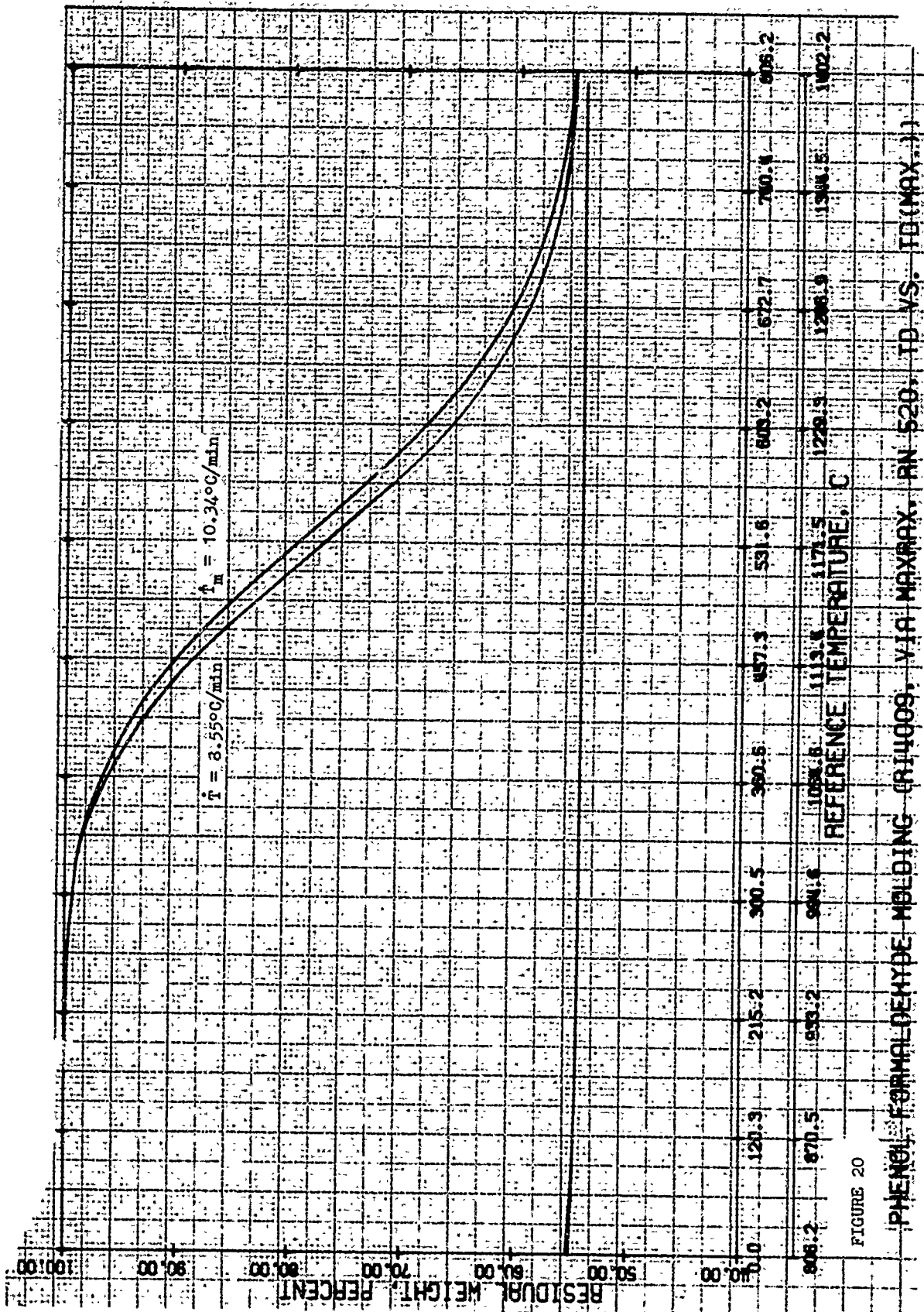


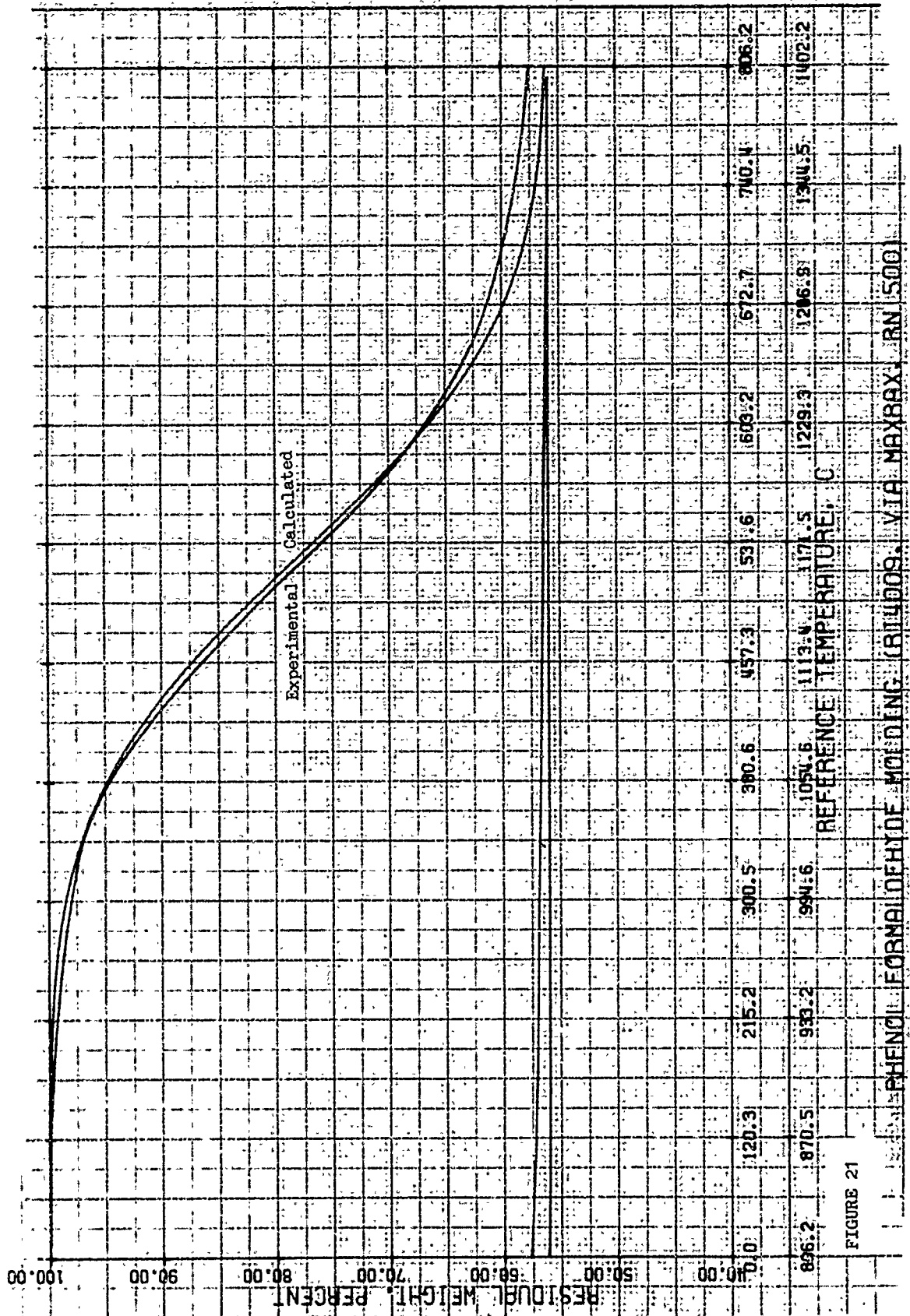
FIGURE 20

PHENOL-FORMALDEHYDE MOLDING (R14009, VIA MAXRAX, RN 520, TD VS. TD(MAX.))

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PART III

APPENDIX I
COMPARATIVE THERMOGRAMS



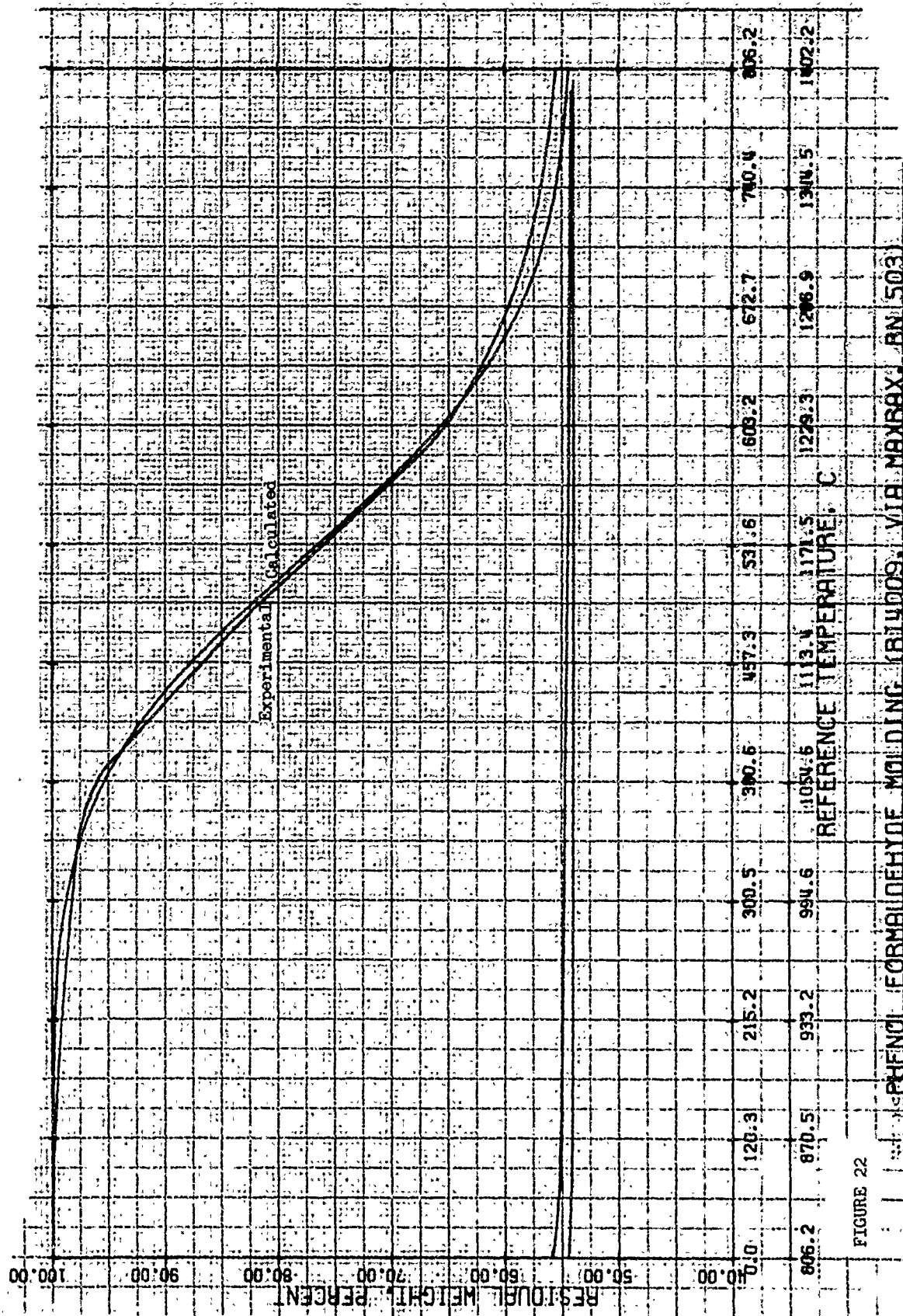
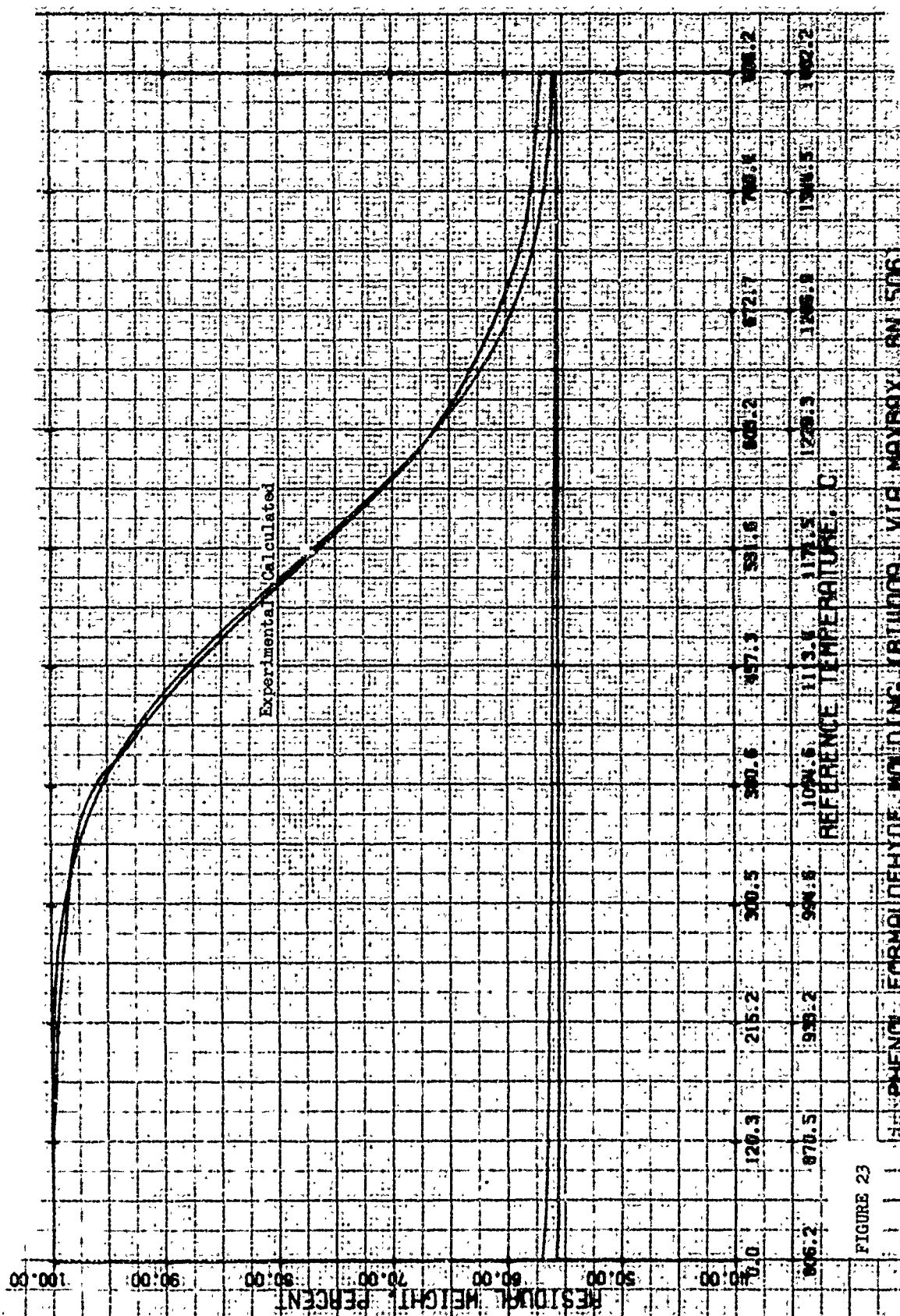
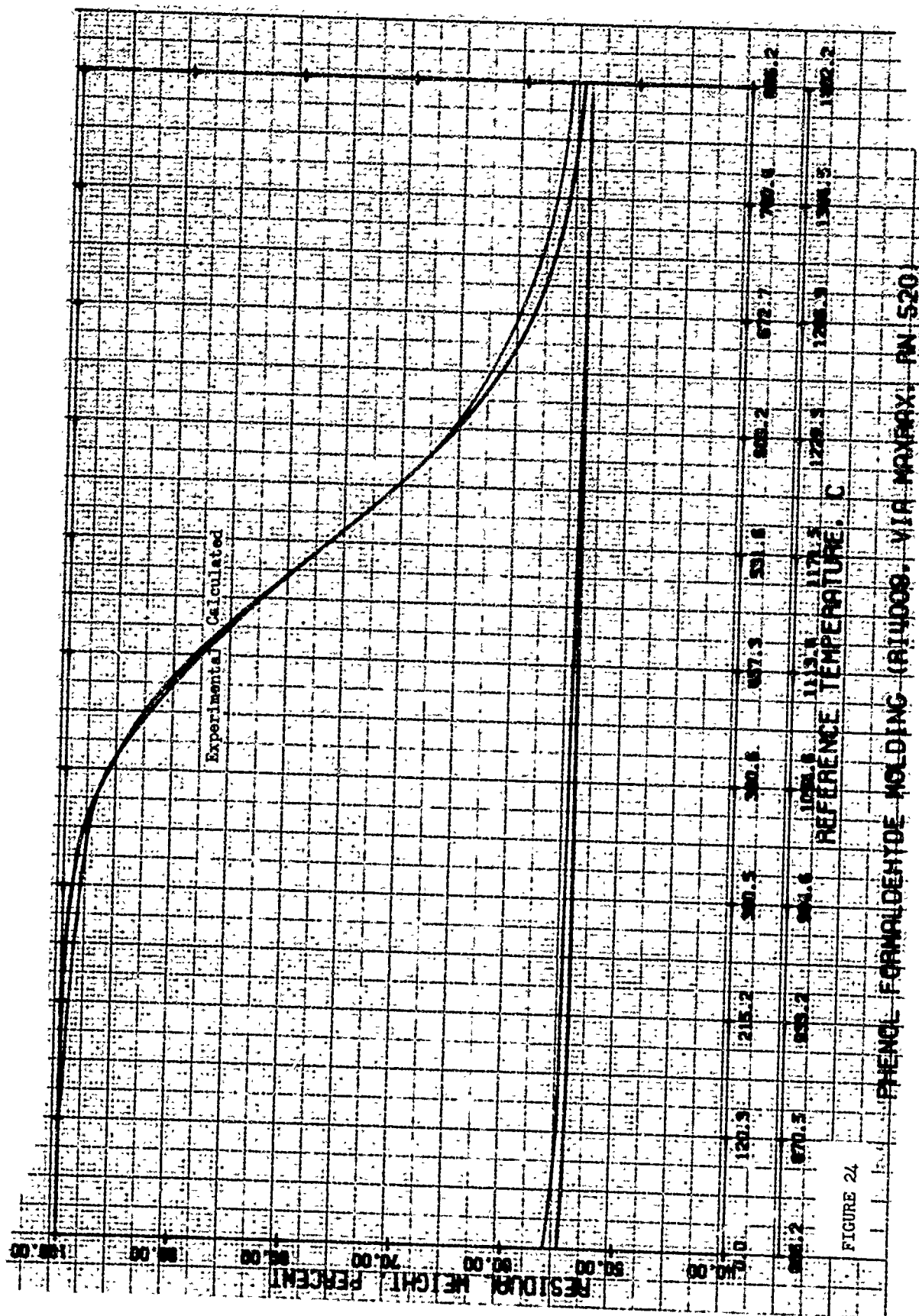
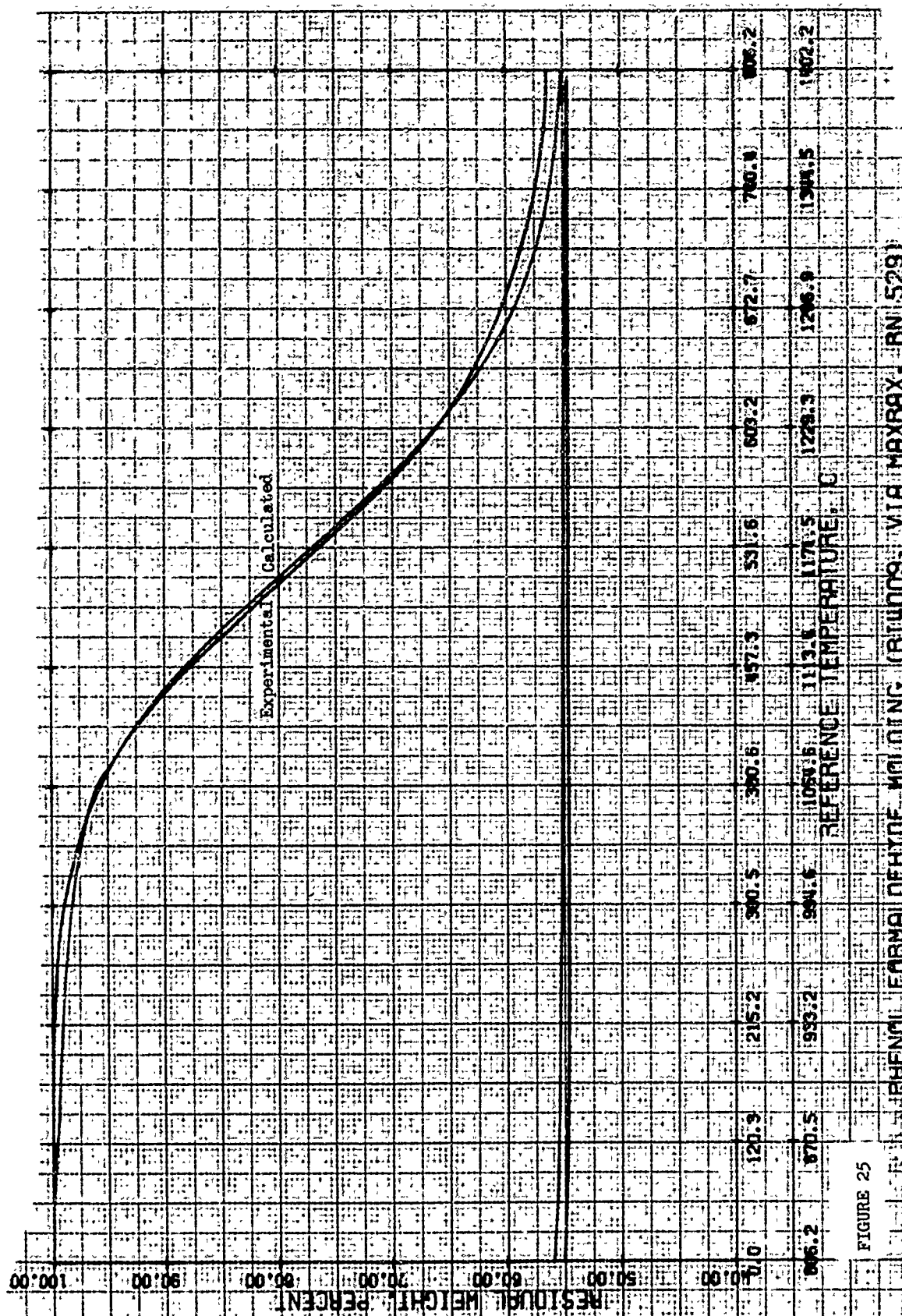


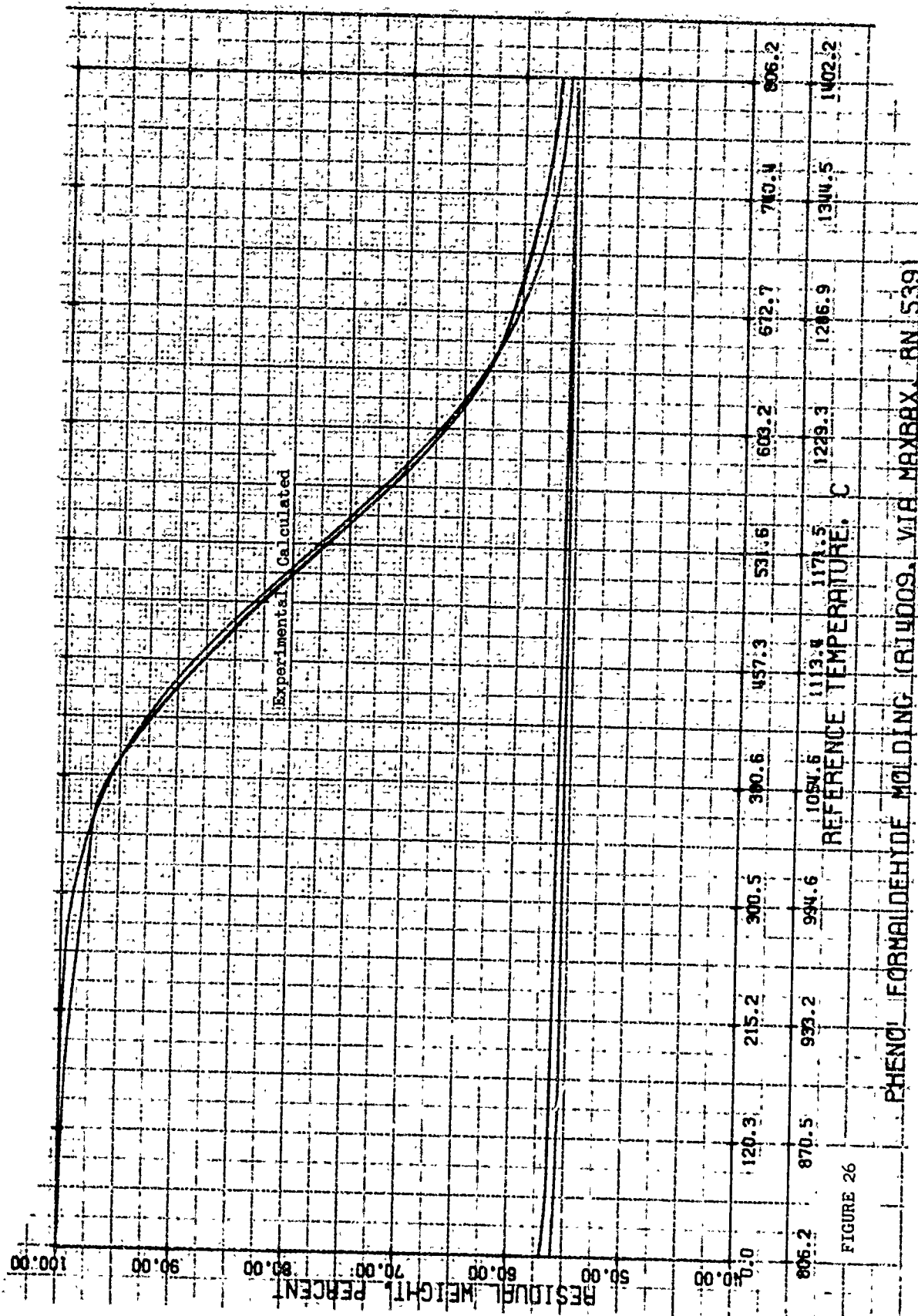
FIGURE 22

PHENOL FORMALDEHYDE MOLDING (B114009, VIA MAXBAX, BN 503)









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PART III

APPENDIX II
EXPERIMENTAL THERMOGRAMS

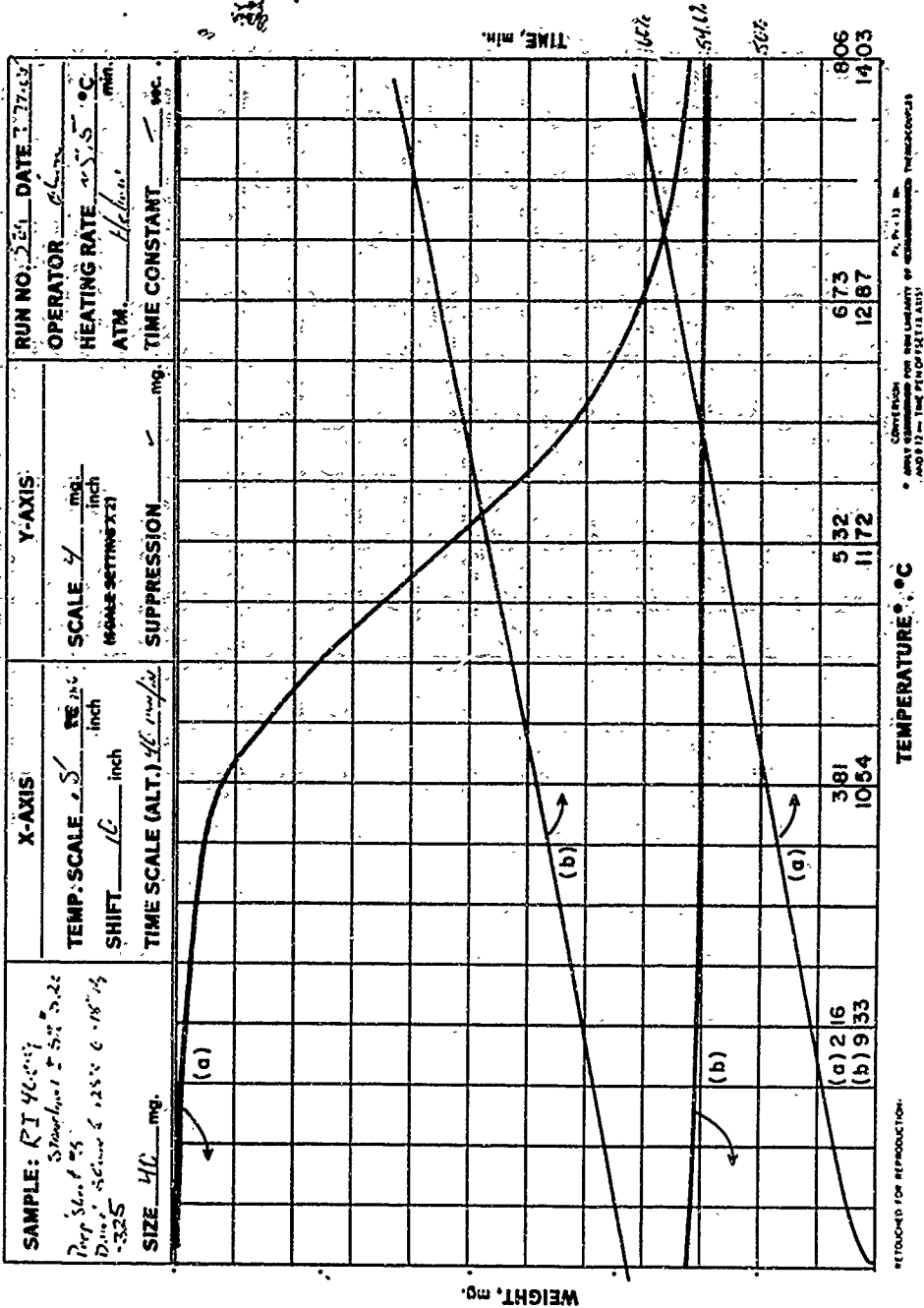


Figure 27. Phenol Formaldehyde Molding (RI4009, RN 529)

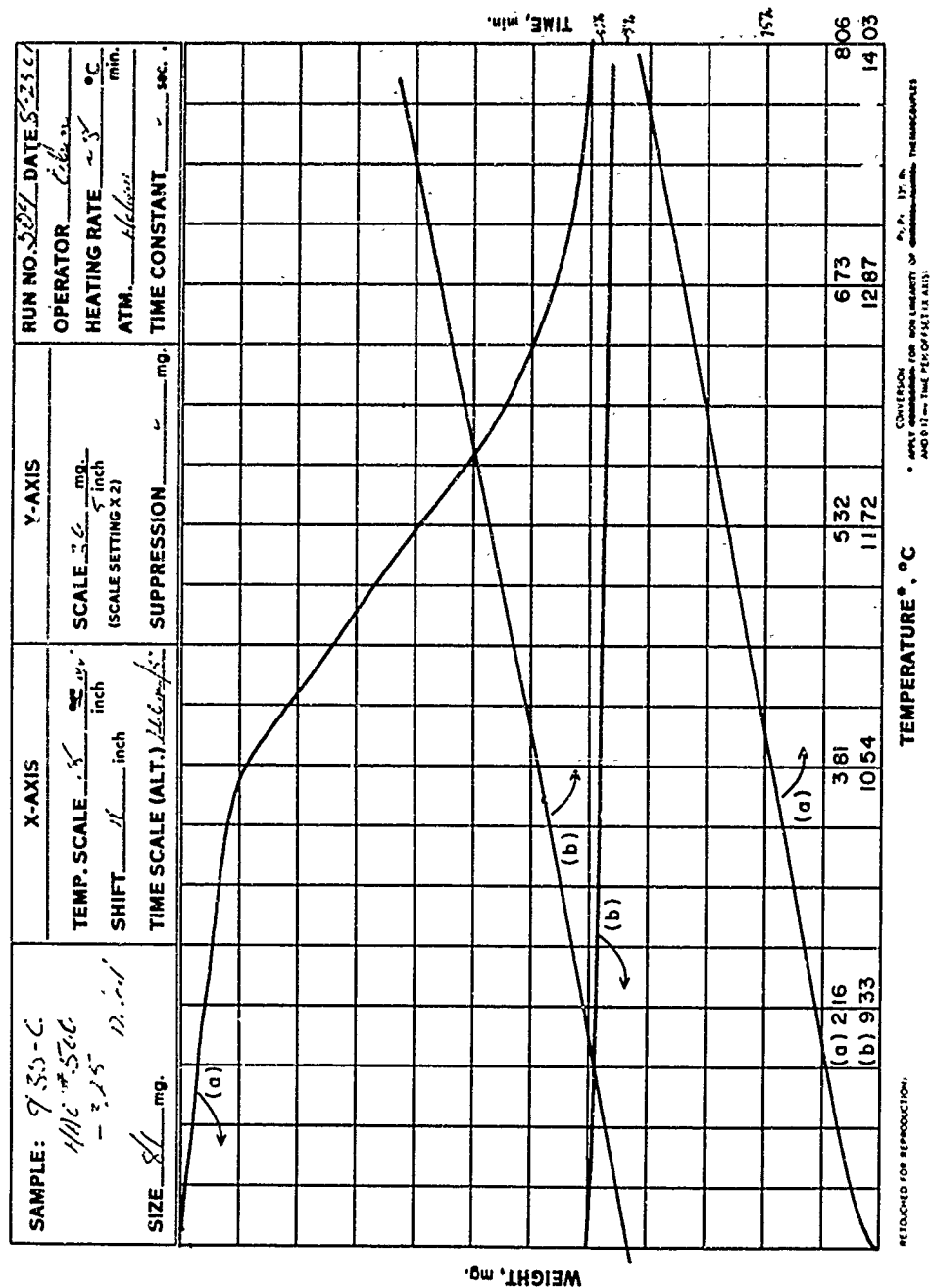


Figure 28. Phenol Formaldehyde/Carbon Cloth (9-35-C, RN 504)

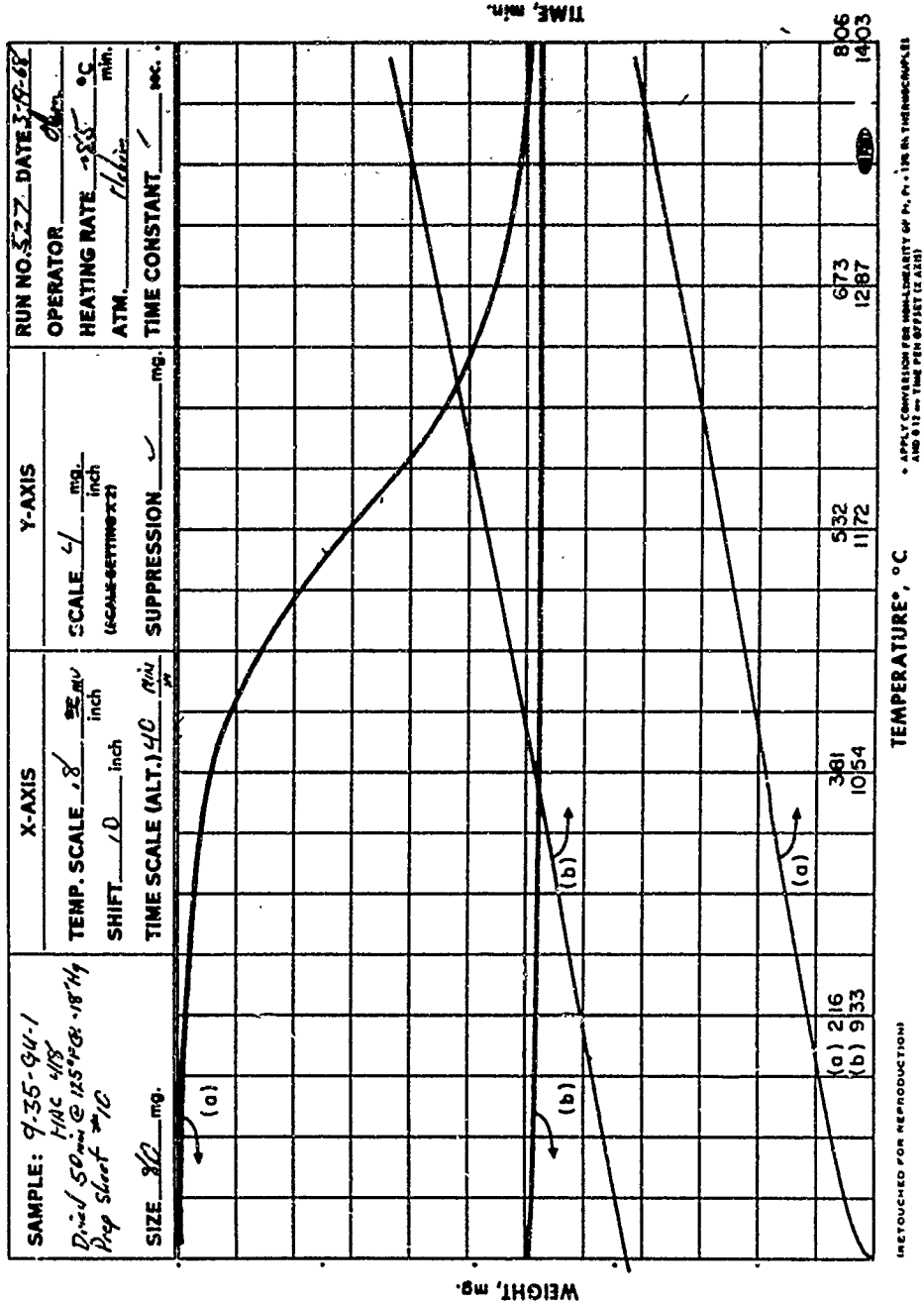


Figure 29. Phenol Formaldehyde/Graphite Cloth (9-35-GU-1, RN 407)

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| 13. ABSTRACT Carbon and graphite cloth reinforced phenolic composites find Air Force ablative thermal protection uses as nose tips, heat shields, and rocket nozzle elements. Weight kinetics are used in predicting the performance of these and related materials. The most general source of the necessary kinetic parameters is thermogravimetry. Kinetic parameters n, A, and E were empirically calculated for the pyrolysis of phenolic molding, phenolic/carbon cloth, and phenolic/graphite cloth materials. The simple model was $-(dw/dt) = w^n A \exp(-E/RT)$ where w = normalized weight, t = time, R = gas constant, T = temperature. The material was first pulverized by a lathe method. A -325 sieve, dried 40 or 80 mg powder was run at 8.5°C/min to 1400°C in a helium purge of 1 liter/min. An integral method computer code and a maximum rate of weight loss method computer code calculated n, A, and E. To define the gross sum of all errors, a third computer code was used to plot thermograms for comparison with the experimental. The empirical kinetic parameters predicted thermograms within 2% residual weight of the parent one. Of three typical bands of disagreement, the largest usually occurred within the third band near 800°C. There was little weight loss beyond 1000°C for any material. The phenolic molding parameters were in good agreement with multiple heating rate and multiple materials results of previous work. | | | |

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|-----|-------------------------------------|--------|----|--------|----|--------|----|
| | | ROLE | WT | ROLE | WT | ROLE | WT |
| | Ablation | | | | | | |
| | Ablative Materials | | | | | | |
| | Carbon Cloth | | | | | | |
| | Graphite Cloth | | | | | | |
| | Kinetics | | | | | | |
| | Kinetics and Mechanisms | | | | | | |
| | Phenolic Resins | | | | | | |
| | Phenol-Formaldehyde Polycondensates | | | | | | |
| | Polymers | | | | | | |
| | Reinforced Plastics | | | | | | |
| | Thermal Analysis | | | | | | |
| | Thermogravimetry | | | | | | |

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